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THE INSTITUTE OF PETROLEUM.

An Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on Wednesday, January 12, 1949, the President, Mr E. A. Evans, occupying the Chair.

The Minutes of the preceding Ordinary General Meeting, held on December 8, 1948, were read, confirmed, and signed.

The Secretary (Mr D. A. Hough) announced the names of new Members and Member Companies who had been elected since the previous meeting.

The President, introducing the authors of the paper to be read, said: We are privileged to welcome Dr Barwell and Mr Milne to discuss with us that very elusive property, kinetic friction. Dr Barwell and Mr Milne are working at the National Physical Laboratory, and they are bound to give us something of very definite interest. I always regard the National Physical Laboratory as a place for very clear thinking, and I am sure the paper will lose nothing of that tradition.

Mr Milne then presented the following paper:—

THE MEASUREMENT OF KINETIC BOUNDARY FRICTION WITH REFERENCE TO SPECIFICATIONS FOR LUBRICATING OILS.

By F. T. Barwell,* and A. A. Milne.*

Summary.

Measurements of kinetic boundary friction are discussed in relation to their utility in characterizing the "oiliness" of a lubricant. It is shown that "oiliness" is not a unique property of a lubricant, but that friction varies widely with such factors as speed of sliding, roughness and hardness of surfaces, and temperature.

Possible methods of specification are discussed, but it is concluded that a generally applicable system will be difficult to devise.

Introduction.

Due to the work of Stanton and others, the importance of "oiliness" in certain lubrication problems has been appreciated for many years. However, the property has so far proved to be so elusive that measurement for the purpose of specification has never become general practice.

This is not altogether surprising in view of the fact that no unambiguous theory exists by which the mechanism of boundary lubrication can be elucidated or the property of "oiliness" related to any physical or chemical concept which can be rigidly defined by reference to the lubricant alone.

Again, in practice we deal with a system comprising two surfaces in

* Engineering Division, National Physical Laboratory.

relative motion with a lubricant between them. The degree of separation will depend not only on the properties of the lubricant, but also on the nature of those surfaces and of their relative movement. Because of the possibility of an interaction (in the statistical sense) between lubricant and surface it would be unwise to consider "oiliness" as a property of the oil alone. Indeed "oiliness" may arise from an interaction (in the physical or chemical sense) between those elements.

It is not the object of the present paper to discuss research into the fundamentals of the subject, but merely to provide a basis for a discussion on the best method of bringing oil specifications into line with the existing state of knowledge of the subject.

The subject will be reviewed on the assumption that any specification for "oiliness" would be based on a test method whereby the lubricating effect of an oil is measured under appropriate sliding conditions and, up to the present day, the coefficient of friction has been regarded as being the most satisfactory criterion for assessing lubricating efficiency as distinct from "extreme-pressure" properties or wear.

In connexion with wear it is necessary to remark that, in some instances,[1,2] it has been found that substances capable of reducing friction between loaded surfaces or of increasing their load-carrying capacity have actually led to an increased rate of wear.

Many machines, particularly those designed primarily for wear testing, operate under conditions of mixed hydrodynamic and boundary lubrication and therefore do not provide consistent evidence of the relative "oiliness" of lubricants of different viscosity. In order to eliminate the effects of viscosity from measurement of friction, it is necessary to ensure that no hydrodynamic effects exist, and this is much more difficult than reference to Reynold's theory would lead one to suppose. In practice it is necessary to work at very low relative velocities of the rubbing surfaces, to apply comparatively high pressures between them, and to shape them so as to minimize any spatial or thermal-wedge action which might occur.

The most difficult feature of the problem is, however, the effect of the nature of the rubbing surfaces on the value of the coefficient of friction, and the paper will be mainly concerned with an attempt to assess the conditions under which variations in such factors as sliding velocity, hardness of surface, temperature, etc., effect the results of friction tests.

Apparatus.

The coefficient of friction between two rubbing surfaces may be determined either directly by measurement of the tangential force or inferentially, as, for example, from the rate of heat generation and therefore temperature rise at the interface.

Direct measurement of the tangential force possesses considerable theoretical advantages over indirect methods. Forrester,[3] in effect, weighs the frictional forces. Of the indirect methods, Schnurmann [4] estimates the frictional forces by observation of the temperature rise of the rubbing surfaces, and Beeck, Givens, and Smith [5] observe the retardation of the surfaces. Other methods of measuring force usually involve some intermediate stage, for example, in the Physikalische-Technische Reichanstalt friction is

measured by the deflection of a heavy pendulum,[6] and many workers, *e.g.*, Deeley,[7] Bowden,[8] Bristow,[9] and Dokos [10] have employed an elastic restraint to one of the sliding surfaces, the deflection of which provides the required measurement of force.

The degree of mechanical restraint of the "stationary" element of a rubbing pair may profoundly affect the nature of the sliding motion, for example, when the conditions are such that the coefficient of friction diminishes as the relative velocity increases. There is thus a velocity term in the expression for the force applied to the elastic system comprising the "stationary surface" and the force measuring restraint applied to it. This term acts in opposition to any damping which may be present in the elastic system. Thus, when the slope of the friction–velocity curve is negative in sign and of sufficient magnitude, energy will be continually

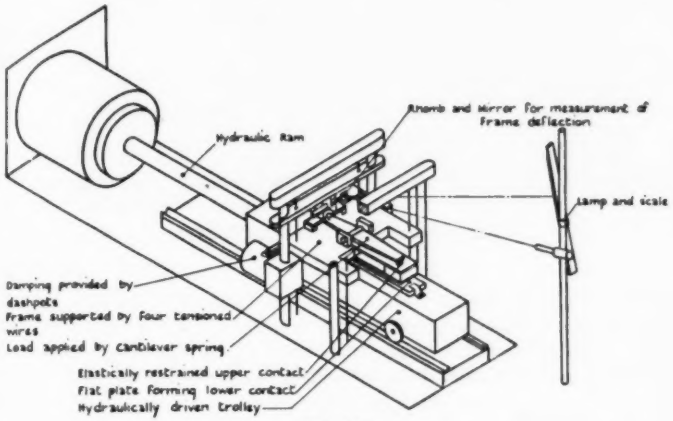

Hydraulic Ram
Knomb and Mirror for measurement of Frame deflection
Lamp and scale
Damping provided by dashpots
Frame supported by four tensioned wires
Load applied by cantilever spring
Elastically restrained upper contact
Flat plate forming lower contact
Hydraulically driven trolley

FIG. 1(*a*).

KINETIC BOUNDARY FRICTION MACHINE. (OPTICAL MEASUREMENT.)

supplied to the system which will oscillate. Such oscillations may be regarded as evidence that the slope exceeds a certain value and therefore as being indicative of imperfect lubrication. However, it may not always be easy to ensure that the inherent damping of a system falls within prescribed limits and because an actual value of coefficient of friction cannot be reliably assessed when the system is oscillating, practice at the N.P.L. has been to follow Bristow [9] in the use of a system which is artificially damped to such an extent that oscillatory motions do not occur. It is then possible to obtain a unique value for coefficient of friction for any given condition of sliding, and providing damping is sufficiently great, the results are not dependent on the characteristics of the measuring system. Most of the results quoted below were obtained by this method, which has been described fully elsewhere [9] and which is illustrated in Fig. 1.

A variation of this system, Fig. 2, has since been devised whereby electric-resistance strain gauges are used to measure directly the tangential force and which are attached in series with rubber blocks which act as an elastic

system embracing springs and dashpots in parallel. The stiffness of the strain-gauge element being large compared with that of the rubber blocks, the system measures, in effect, the force applied to an elastic system instead of the deflection of such a system as the result of the application of that force.

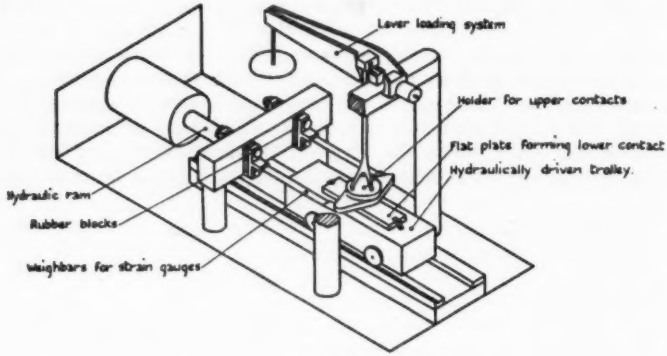


FIG. 2(*a*).

KINETIC BOUNDARY FRICTION MACHINE. (ELECTRICAL MEASUREMENT.)

FACTORS AFFECTING FRICTION.

General.

Factors which are known to affect the coefficients of friction between rubbing surfaces include velocity, temperature, load, area of contact, lubricant, and the material, hardness, curvature, and finish of the surfaces. Other factors, such as the humidity and nature of the surrounding atmosphere,

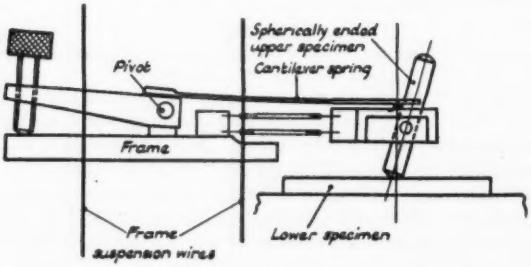


FIG. 3.

DETAILS OF SUSPENSION OF UPPER SPECIMEN.

and the subsurface or bulk properties or the materials, have also been suspected at some time or other as affecting results, but this evidence is not sufficiently extensive to enable reliable conclusions to be drawn. This is a formidable list of factors, but they are not all of equal or practical importance.

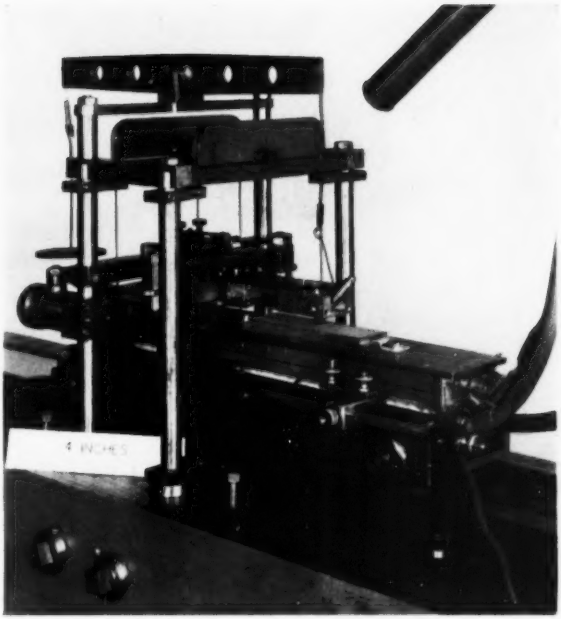


FIG. 1(*b*).

KINETIC BOUNDARY FRICTION MACHINE. (OPTICAL MEASUREMENT.)

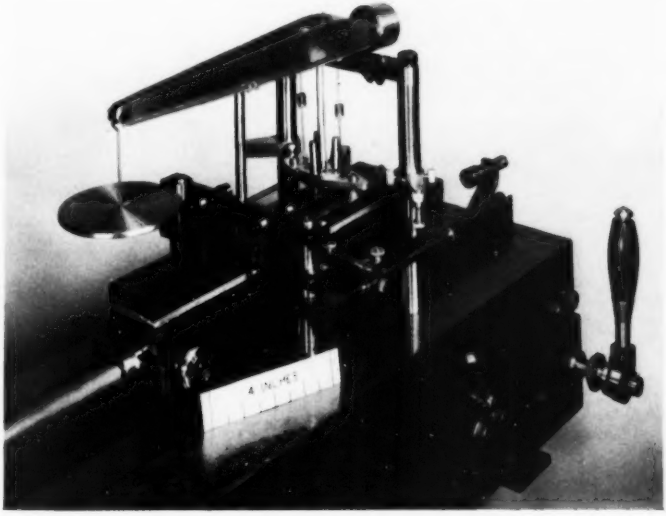


FIG. 2(*b*).

KINETIC BOUNDARY FRICTION MACHINE. (ELECTRICAL MEASUREMENT.)

[*To face p.* 458.

Effect of Velocity of Sliding.

Early workers divided friction under boundary conditions into two categories, static and kinetic boundary friction, with the static value usually higher than the kinetic and the kinetic value independent of velocity.[11] This view is now recognized as being an over-simplification, as kinetic boundary friction may vary widely over the velocity range 0 to 1·0 cm/sec. Fig. 4 shows three friction–velocity curves which may be regarded as being representative of the three forms met with in practice. Bristow [9] has reported a gradual transition from type (*a*) to type (*c*) as different proportions of oleic acid are added to mineral oil.

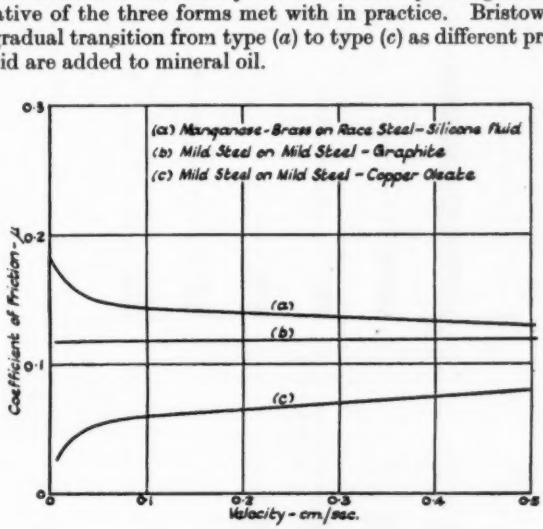


FIG. 4.

TYPICAL COEFFICIENT OF FRICTION–VELOCITY CURVES.

Above a velocity of about 1 cm/sec, friction varies little with velocity until high sliding velocities are reached. At this stage it is probable that Reynolds lubrication conditions begin to affect the results.[12,13] Friction then becomes dependent on other factors than "oiliness."

Effect of Material of Sliding Contacts.

Fig. 5(*a*) shows the results of friction tests on a number of materials rubbed together in the presence of two different lubricants, oleic acid and highly refined mineral oil. The coefficient of friction at a velocity of 0·01 cm/sec is shown black for oleic acid and white for the mineral oil. The materials are arranged in ascending order of hardness, although this may not be the relevant parameter physically. It will be noted that the difference between materials may be large compared with the difference obtained when different lubricants are applied to any one material.

Fig. 5(*b*) shows a series of dissimilar materials, in fact, the materials of Fig. 5(*a*) sliding on smooth tungsten carbide, and tungsten carbide sliding on those materials. It will be noted that there is no characteristic difference

between the sets of results and that change of lubricant now has a considerable proportionate effect on the total friction.

Fig. 5(*c*) shows the same material sliding on rough tungsten carbide. Here the nature of the softer material appears to affect friction considerably

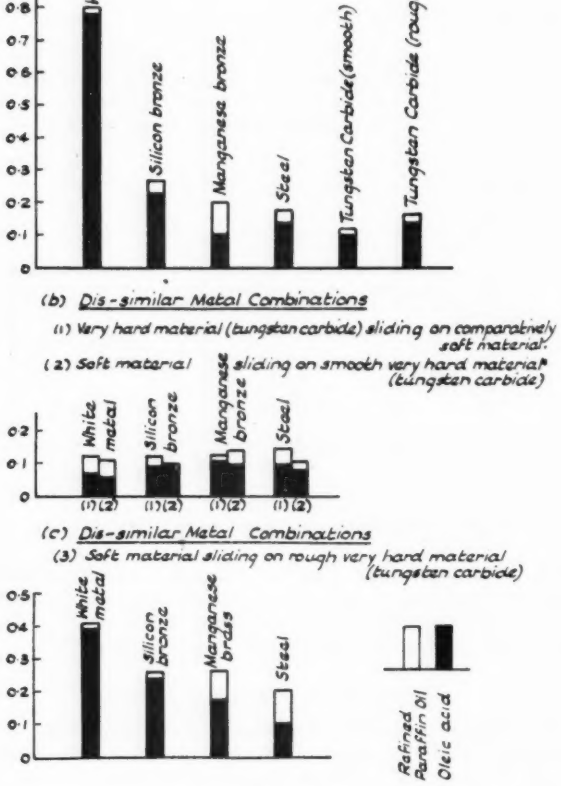


FIG. 5.

COEFFICIENTS OF FRICTION FOR VARIOUS MATERIAL COMBINATIONS AT 0·01 CM/SEC, 20° C.

and the behaviour is qualitatively similar to that noted when similar metals slide one over the other. It will be clear from comparison of Figs. 5(*b*) and (*c*) that under some conditions of test, roughness may have an appreciable effect on friction, and this will be discussed further in Section 4.

Effect of Temperature.

Fig. 6 shows some typical friction–velocity curves for measurements made at 25° and 100° C. Two lubricants, A, a silicone fluid and B, a good mineral-base lubricating oil are compared. Fig. 6(*a*) shows the behaviour when hard steel ($H_{D30} = 750$) slides on hard steel. For the silicone A,

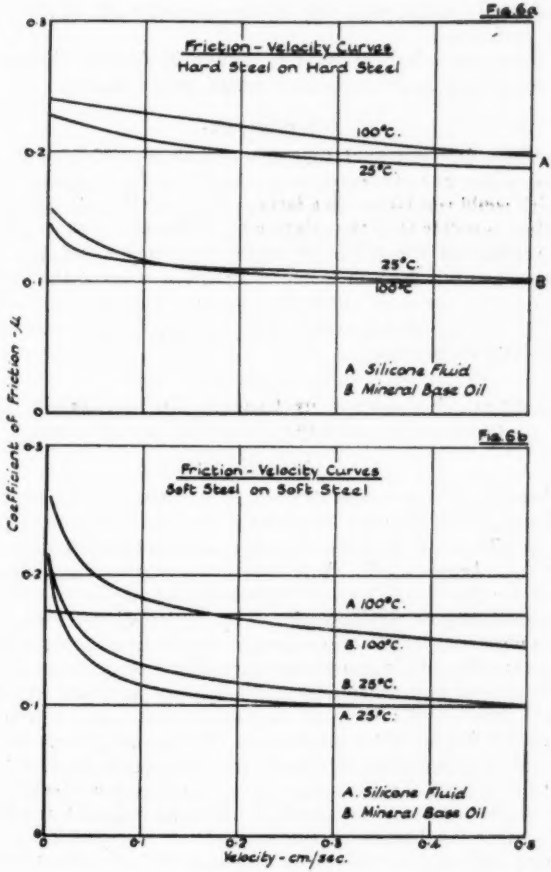


FIG. 6.

friction is shown to increase with temperature, but there is little difference between temperatures for the mineral oil, B, except at very low velocities. Fig. 6(*b*) shows the same two lubricants tested between soft steel ($H_{D30} = 180$) sliding on soft steel. It will be noted that the form of the friction–velocity curve of the combination lubricated with fluid A is profoundly altered.

The change in frictional behaviour with temperature may be discon-

tinuous, for example, Frewing [14] found that a change from smooth to erratic sliding occurred at a distinct temperature, which he describes as the "transition temperature." Bowden [15] has shown such discontinuities when solid hydrocarbon films are heated through their melting points, and has suggested that other discontinuities may be identified as occurring at the melting point of intermediate products resulting from chemical combination of the lubricant with one or more constituents of the material of the sliding surfaces.

A particular example of a sudden change in friction characteristic is described more fully in the section on experimental results.

Other Effects.

Tingle [16] has demonstrated that the combined action of atmospheric oxygen and water was necessary to produce a surface film on "reactive" metals which could combine with a fatty acid to provide effective lubrication. It is therefore possible that the relative humidity at the time of test or the moisture content of the lubricant under test may affect the results of friction experiments. No conclusive evidence exists that the variations in relative humidity normally encountered in a laboratory are sufficient to affect results to a significant extent, but this may be the cause of many so far unexplained variations.

Experimental Assessment of Certain Factors affecting the Coefficient of Kinetic Boundary Friction.

General.

It has been found extremely difficult to compare the results of workers using different test conditions, because the number of factors which may be expected to affect the results is so large, and because reproducibility of results is not always good. A research programme has therefore been initiated at the National Physical Laboratory which has been designed so that the results may be rigidly analysed by statistical methods. There are three main objectives of this programme. In the first instance it is desired to observe the effect of the many experimental variables, secondly, to enable the significance of any differences to be reliably assessed, and finally, to provide a comprehensive array of comparable data against which certain theories of the fundamental mechanism of boundary lubrication may be checked. It is hoped later to extend the programme to a wide range of substances of known chemical composition so that the effect of molecular structure on friction may be assessed under all relevant conditions, and molecules giving low friction be synthesized.

This work has only recently been commenced, but some data is already available which is relevant to the present subject, and is therefore outlined in the following paragraphs. The data so far obtained relate to the variations that surrounding factors produce in the friction between surfaces of a given material when lubricated by a single substance.

Experimental Design.

The factors which might possibly affect the friction between rubbing surfaces have been enumerated earlier. Owing to the possibility of statistical

interaction between the variables, the experiment has been based on a factorial design, the number of levels for each factor being kept to a minimum consistent with the range to be covered.[21]

The material for the rubbing surfaces in the initial programme was chosen to be a carbon steel (1·18% C) capable of being hardened from $200H_{D30}$ to $1000H_{D30}$.

So far, the experiment has been performed for only one substance as lubricant, methyl stearate. This substance was prepared by the Chemical Research Laboratory and is an intermediate product arising from the preparation of pure stearic acid and some of its metallic salts which are required for the full investigation. Methyl stearate is a solid, crystalline substance at room temperature, with a melting point of 39·5° C.

Each individual test produced a curve of friction against velocity over a range from 0·0015 cm/sec to 0·6 cm/sec. The velocities could not be closely controlled, but could be accurately measured. Each test involved measurement of friction at eight discrete velocities, and was replicated four times on different specimens. Through the thirty-two different values obtained and plotted, the best curve was drawn, from which friction coefficients at specific velocities could be interpolated.

For each factorial combination friction–velocity curves were obtained at six thermostatically controlled temperatures between 25° and 150° C at 25° C increments. These were arranged in ascending–descending order to minimize possible errors due to progressive thermal changes in the lubricant.

The lower surfaces were prepared by grinding followed by wet random abrasion with powders of different degrees of fineness. Two degrees of surface finish, "smooth" and "rough", were desired in order to assess the range of importance of this variable. Surfaces were examined with a "Talysurf" instrument and by the Guild [18] optical method before test. The degree of reproducibility may be assessed by reference to Table I. It will be noted that the surfaces show no directional properties and, while different in degree, are similar in kind.

The standard load applied between the rubbing surfaces was 8 lb, but certain conditions of test (*i.e.*, 25° and 150° C) were repeated with an applied load of 2 lb.

The upper surfaces were machined as rods presenting spherical ends and were turned in a lathe and then finished with 4/0 emery paper. Some of them were hardened before the final polish to enable the effect of hardness of the upper contact to be assessed. Three radii of curvature were provided. The normal radius as used hitherto was 0·5 cm and two others, a "small" radius of 1·5 mm, and a "large" radius of 8 cm, provided extremes of curvature.

The upper contacts were arranged in an inclined position as shown in Fig. 3. There were two reasons for this arrangement. In the first place, when the parts were being turned in a lathe, the relative velocity between the tool and the work at the centre is zero and therefore pure cutting cannot occur. The condition of the metal and the precise form of the component at this point are therefore not readily determinable. By inclining the axis of the rods during the test this point cannot affect the experiments. Secondly, there is a distinct risk that, during a friction test, the form, or degree of roughness, of the moving contact will be modified with consequent effect

TABLE I.

Measurements of Surface Roughness.

	Plate.	Guild optical method, S/T ratio.			"Talysurf" readings, $H_{av.}$		
		Longitudinal.	Transverse.	Mean.	Longitudinal.	Transverse.	Mean.
"Rough" Surfaces.	1	0·022 0·016 0·015	0·019 0·021 0·016	0·018	42–52	44–54	48
	2	0·022 0·031 0·025	0·026 0·030 0·027	0·027	50–55	45–50	49
	3	0·016 0·020 0·016	0·016 0·016 0·014	0·016	46–58	48–54	51
	4	0·013 0·021 0·016	0·022 0·018 0·020	0·018	45–50	45–50	47
"Smooth" Surfaces.	5	0·729 0·667 0·718	0·686 0·673 0·712	0·698	2·2–2·5	2·0–2·4	2·3
	6	0·726 0·693 0·801	0·716 0·682 0·777	0·733	2·1–2·2	2·2–2·7	2·3
	7	0·742 0·742 0·827	0·739 0·725 0·806	0·764	2·0–2·6	1·7–2·2	2·2
	8	0·761 0·726 0·763	0·735 0·700 0·774	0·743	1·8–2·4	2·0–2·4	2·1

upon the results. Whilst no correction for this effect can be made during an individual test, it is manifestly prudent to commence each test on a fresh surface. An economical method of doing this is to rotate the inclined test piece between each test so as to present a fresh area for each individual test.

Method of Test and Cleaning of the Surfaces.

Cleaning of Surfaces.

The cleaning of the surface before application of the lubricant is generally recognized to be a factor of great importance in aiding reproducibility of results. The subject of surface cleaning has been discussed by many workers, including Hardy,[11] Forrester,[3] Johnson, Swikert, and Bisson,[13] Fogg and Hunwicks,[17] and Groves.[20]

In the present series of tests the following method of cleaning the prepared surface has been adopted and has been found to give satisfactory results :—

(i) the surfaces were scrubbed with cotton-wool in caustic soda solution to remove all traces of grease, grit, and dirt;

(ii) the surfaces were rinsed in water, and when the surfaces were capable of being completely wetted they were assumed to be clean;
(iii) the surfaces were dried with acetone, which was allowed to evaporate.

During these operations and subsequently, the surfaces were untouched by hand. The specimens were mounted in the machine, and the lubricant was applied as soon as possible after the final drying.

Method of Test.

For each combination of the other factors, a complete set of friction–velocity data at the six temperatures and two loads was obtained. The combination was replicated on four different upper and lower specimens, so that possible differences between plates would be evenly distributed over all the factors. By rotating the upper contact about its inclined axis, and shifting the lower plate, fresh surfaces were used for the runs at each temperature and load. For each run down each plate the friction was measured at eight discrete velocities. To avoid errors due to possible changes in the upper surface during the run, these velocities were varied in a random manner.

For each combination of the controlled factors a set of thirty-two friction–velocity values was thus obtained. These were plotted and the best curve drawn through them. By examination and comparison of these curves, or of interpolated values of coefficient of friction at specific velocities, the effects of the various factors or conditions of test for the given material–lubricant combination may be observed and assessed.

Experimental Results.

General Observations on Observed Results.

The complete set of data for this factorial experiment presents a perplexing array of no less than ninety-six friction–velocity curves. A full statistical analysis of the results has not yet been completed, but certain trends may be immediately distinguished. Though considerable interactions occur between the factors, it is expedient to consider their effects separately, so far as is possible, with reference to selected examples. Owing to the scatter of results and the incompletion of tests of significance, differences between curves corresponding to differences in coefficients of friction of less than about 0·01 should not necessarily be regarded as being significant.

Effect of Factors Likely to Vary in Service.

Effect of Velocity. The effect of velocity upon friction shows considerable interaction with the other factors. Under appropriate conditions friction–velocity curves of all the shapes previously mentioned may be obtained. Examples of these curves are shown in Fig. 7. The majority of curves showed the falling characteristic of example (*a*), but a few approximately level or rising curves were obtained as in examples (*b*) and (*c*).

Effect of Temperature. While the influence of temperature also cannot be considered without any reference to the other factors, the curves shown in

Fig. 8 may serve to indicate the magnitude of the effect that may be obtained. At a temperature below the melting point the coefficient of

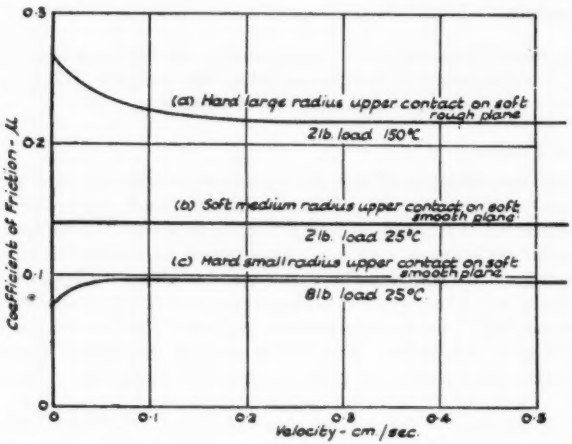


FIG. 7.

TYPICAL FRICTION–VELOCITY CURVES.

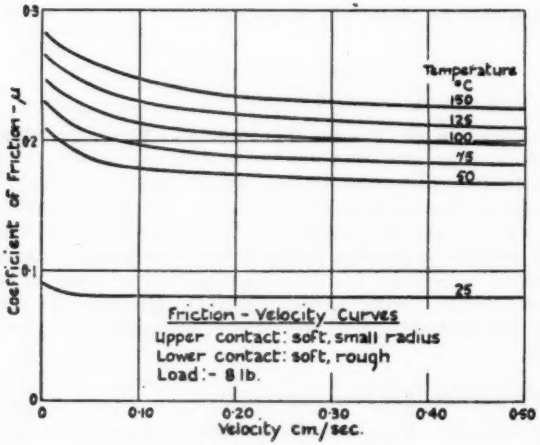


FIG. 8.

friction, in the example, dropped from a value of 0·09 at very low velocities down to a steady value of 0·08 at about 0·5 cm/sec. Immediately above the melting point, however, the friction greatly increased over the whole range of velocities, to corresponding values of 0·23 and 0·17, and grew steadily

greater as the temperature was increased. Plotting friction against temperature for this set of curves at specific velocities, curves of the form shown in Fig. 9 were obtained. There was a sharp discontinuity around and about the melting point, but above this the friction appears, to a first approximation, to vary linearly with temperature.

At temperatures above the melting point of the lubricant, friction–velocity curves in all cases showed a falling characteristic, the characteristic being smallest for the low-temperature smooth surfaces and greatest for some high-temperature smooth surfaces. At the temperature below the melting point the curves showed all three characteristics depending on the conditions. In general, the smooth surfaces gave level or rising characteristics, and the rough surfaces level or falling characteristics. It is to be regretted that the lubricant was such as to enable only one temperature below the melting point to be investigated.

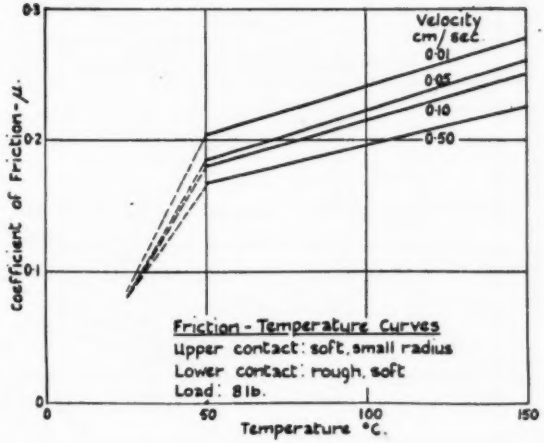


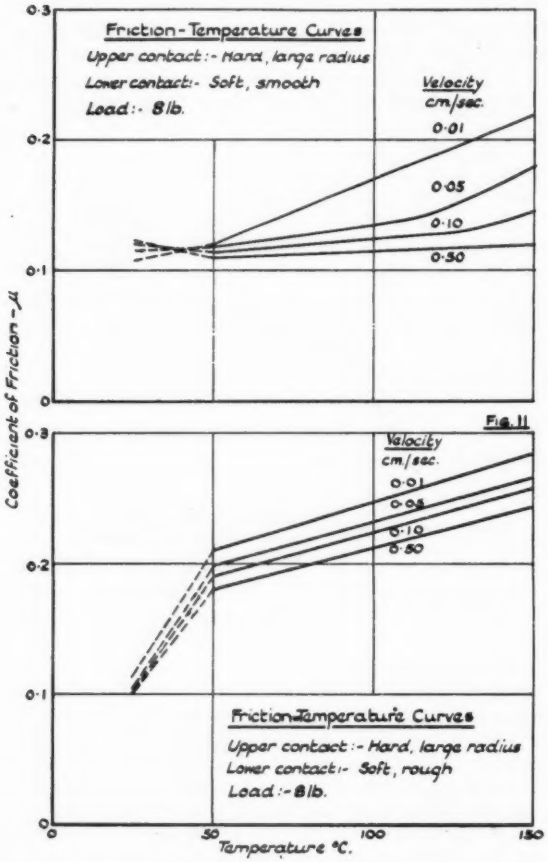
FIG. 9.

Effect of Surface Finish of the Lower Plate. A typical example of the effect of surface roughness that was obtained is given by comparison of the friction–temperature curves in Figs. 10 and 11. The only difference between the conditions for these two sets of curves is in the roughness of the lower plate. At temperatures below the melting point of the lubricant the smooth surface showed a rising characteristic curve, while the rough surface showed a falling characteristic. At high velocities the smooth surface gave a slightly higher friction than the rough, while at low velocities the rough surface gave a slightly lower friction. Differences, however, were not great. Above the melting point the effect of roughness was very marked. For the rough surface the friction was high throughout, values ranging from 0·16 to 0·30, with a sharp rise in friction with decreasing velocity and progressive worsening as temperature was increased. For the smooth surface the friction was considerably less throughout. At high speeds there was no appreciable change with temperature, values remaining fairly constant at

just above 0·10, but at low speeds there was increasing tendency for the curves to turn up as temperature was increased.

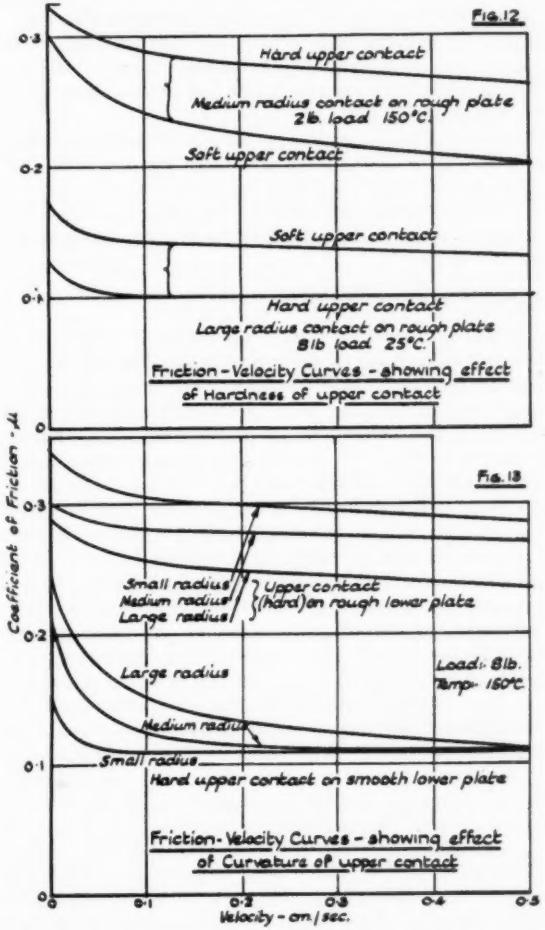
Under other conditions of test, similar differences were found between smooth and rough surfaces. At temperatures above the melting point the

FIG. 10.



rough finish gave coefficients of friction substantially greater than the smooth under all conditions. Differences ranged from 0·04 to 0·17, being in general more marked for small radii of curvature, for the higher velocities at high temperature or the low velocities at low temperatures, and for the hard upper contacts. At temperatures below the melting point the differences were small. The smooth surfaces tended to give curves with a

level or rising characteristic, while the rough surfaces gave curves with a level or falling characteristic. For the hard upper contacts at high velocities the rough surface gave the lower friction, while at very low velocities the smooth surface gave the higher friction. This tendency to cross over was less marked for the soft upper contacts than for the hard upper contacts.



The small radius of curvature shows a small effect, the medium radius barely shows it, while for the large radius the rough surface gives an appreciably higher friction throughout.

Effect of Hardness of the Upper Contact. The effect of hardness of the upper contact is again closely inter-related with the other factors, and is illustrated in Fig. 12. Certain tendencies may, however, be noted. At

temperatures above the melting point, for the rough-surface finishes of the lower plate at all radii of curvature, and at all velocities, the harder upper contact gave coefficients of friction greater than the softer contact, differences being most marked for the smallest radius of curvature and at the highest temperature. For the smooth-surface finish the harder upper contact gave higher coefficients of friction than the softer contact at temperatures just above the melting for all radii of curvature and all velocities. For the highest temperatures, however, whereas for the large radius the hard gave higher friction than the soft, the medium radius showed no appreciable difference, and for the small radius at low velocities the soft contact gave a higher friction.

At temperatures below the melting point, for the smooth surface, the hard contact gives a higher friction for the large radius, little difference for medium radius, and slightly less for the small radius. For the rough surface the reverse effect obtains. The harder contact gives a higher friction for the small radius, slightly less for the medium radius, and much less for the large radius.

Effect of Factors Peculiar to the Method of Test.

Effect of Radius of Curvature of the Upper Contact. Typical comparisons between differing radii of curvature are shown in Fig. 13, though the interaction with other factors is again complex. For the rough surface finish, at temperatures above the melting point, decreasing radius of curvature led to a rise in friction, the effect being more pronounced for the harder contacts, and at the lower velocities. Below the melting point there was little difference between small and medium radii (for the hard contact the medium radius had perhaps a slightly lower friction), but the large radius of curvature showed a marked rise, the effect being greater for the soft contact.

For the smooth finishes, at temperatures well above the melting point, decreased radius of curvature was accompanied by a fall in friction, particularly for the hard contact at low velocities. As the velocity increased or temperature decreased the effect became less pronounced. For the soft contacts the differences could not be regarded as significant. At temperatures below the melting point the medium radius of curvature gave slightly lower friction than the small radius, but the large radius gave an increased coefficient, the effect being more pronounced with the softer upper contact.

Effect of the Applied Load. The effect of the magnitude of the applied load varied considerably with the other factors. The differences were in all cases comparatively slight, giving changes of coefficient over a range from $-0{\cdot}02$ to $+0{\cdot}04$. In general, the lower load gave rise to a slightly higher coefficient of friction, this rise being rather more pronounced for the soft upper contacts than for the hard. At high temperatures at low velocities and at low temperatures at high velocities increased roughness increased the ratio of the coefficient of friction at the low load to the coefficient of friction at high loads. On the effect of load at other interactions it would be unwise to discourse without a full analysis of the results.

The effects of the factors previously mentioned do not appear to be altered by change in load, differences being merely of degree rather than of kind.

Conclusions from the Experimental Results.

The results of this experiment may serve to show how rash it is to attempt generalizations from limited data on coefficient of friction. By suitable selection of factors almost any conclusion may be reached. As an example of the sort of misleading conclusion that might be drawn, values of coefficient of friction obtained at, say, 0·5 cm/sec for the large radius hard upper contact on a smooth plate and at various temperatures (see Fig. 10), might lead one to the general conclusion that temperature had little effect on friction! Until the theories of the mechanism of boundary friction and the reduction thereof are adequate to explain all experimental data only a complete investigation of a lubricant–material combination in this manner can be relied on to give the whole story of its friction properties.

Method of Representation of Results.

It will be clear from the foregoing that it is impossible to determine a single number which will be representative of the " oiliness " of a lubricant even if sufficiently representative standard surface conditions may be found. If coefficient of friction be quoted at some arbitrary velocity, different lubricants may be placed in a different order of merit according to the velocity so selected. Again, in many practical uses of a lubricant variation with temperature must be taken into account. Presentation of separate friction–velocity curves for each of a series of temperatures may present a somewhat perplexing array. An additional disadvantage of this method of presentation is that reproducibility of results is seldom good, and it is often difficult to decide on the best form of curved line to put through a series of points; particularly at the lower velocities where curvature is usually marked.

A purely empirical method of representation is to plot log coefficient of friction against log velocity and to draw the best straight line between the points. This appears to fit most data to a first approximation over the velocity range 0·005 to 0·05 cm/sec, and interpolation can be made with much more confidence than when an estimated curve is used. Results can then be quoted at two arbitrarily determined velocities so that a fair approximation of the result is given by two numbers.

The drawing of the best straight line connecting the points is equivalent to assuming that the variation of coefficient of friction with velocity is governed by the law

$$\mu = \mu_0 \, (v/v_0)^{\gamma}$$

where μ_0 is the coefficient of friction at some arbitrarily determined velocity V_0. The μ_0 may be determined from the vertical intercept of the line corresponding to velocity V_0 and γ from the slope of the line. γ may be referred to as the " velocity index " of the lubricant–surface combination, and its sign will determine whether or not this combination will encourage smooth sliding.

An alternative is to quote two values for coefficient of friction corresponding to two arbitrarily determined velocities. When this is done it is somewhat difficult to appreciate the significance of the differences in friction in relation to the absolute values. A third method is to quote the value at

one velocity and the ratio of that value to the value at another velocity. This is not dissimilar in principle from the first method.

The essential requirement is that a standard method of interpolation should be adopted, and the log-regression line appears to be the most rigid solution at present available.

Requirements for a Specification.

Whilst there is some evidence to suggest that, by a judicious selection of test conditions, it may be possible to devise a test which would place lubricants in an order of merit which was representative of general conditions in use, an exhaustive investigation involving many combinations of material and lubricant would be necessary before this could be asserted with confidence. It is probable, for example, that, where the efficiency of lubricants lies not in the substances themselves but in the nature of the products of their chemical reaction with the sliding surface, different surfaces having different degrees of chemical reactivity, may cause the order of merit of two lubricants to be reversed.

It would appear wiser therefore for a number of specifications to be drawn up each being related to a specific industrial application and restricted to a comparatively narrow range of materials. Examples of such categories might be as follows: oils for lubricating pistons (cast iron on cast iron), automobile bearings (hardened steel on leaded bronze), gears (hardened steel on hardened steel), or general bearings (mild steel on white metal). Temperatures of test could be selected based on operating conditions, and it would be relatively easy to specify materials which would place oils in a true order of merit when considered in relation to the restricted range of the particular application.

The selection of the method of preparation of the test surface requires careful consideration. It is naturally desirable that this surface should be representative of practical conditions and yet capable of easy reproduction in the laboratory. These requirements are contradictory, inasmuch as it would be manifestly uneconomic to instal machine tools of the production type in every oil-testing laboratory.

A final preparation by lapping or polishing with abrasive cloth after machine grinding appears to be the most promising solution, although care should be exercised in avoiding directional effects.[19]

It would appear that an intermediate degree of surface roughness should be selected for a standard test, because whilst a certain degree of roughness may serve to emphasize the difference between good and bad boundary lubricants, excessive surface roughness obscures that difference.

A possible inexpensive solution to the problem of providing an easily prepared standard surface consists of mounting a portable grinding machine on the testing machine itself, using the hydraulic drive of that machine to provide a closely controllable fine feed. This method is being developed at the N.P.L., but has not been in use sufficiently long for reliable conclusions to be drawn.

The selection of the relative position of the two components of the sliding pair also requires careful consideration. Because the surface presented by the stationary contact is continuously worn, whereas the moving surface

continually presents fresh material, it is desirable for the upper contact to be made of the more durable material. Some justification of this view can be derived from consideration of what may occur when two components, one hard and the other soft, rub together in an actual mechanism. When new, the surfaces will touch at a few points only, the asperities of the harder surface being pressed into the softer material. As wear takes place, greater conformity will be brought about, but the harder surface will retain its original imperfections of form to a greater extent than the softer surface. These protuberances may then be regarded as sliding over the softer material in the same manner as the upper spherically ended contact in the kinetic-friction machine slides over the lower surface.

Conclusions.

The large number of apparently disconnected factors which affect the measured value of the coefficient of kinetic boundary friction renders the formulation of a general specification a matter of great difficulty. The present paper has been confined to experimental facts, as it was considered premature to introduce theories of the underlying mechanism of boundary lubrication into the discussion. It is possible, however, that a sufficiently general theory would enable the number of parameters to be materially reduced and the problem of specification considerably simplified. Therefore there is every justification for continued research into the problem, even though such work may not have the production of a specification as its main objective.

Finally, it must not be overlooked that, under mixed conditions of lubrication, it is possible that such factors as thermal expansion, viscosity–pressure effects, etc., may be as important in reducing friction and wear as would be a low coefficient of kinetic boundary friction.

Acknowledgment.

The work described above has been carried out as part of the research programme of the National Physical Laboratory, and the paper is presented by permission of the director of the laboratory and the director of Mechanical Engineering Research D.S.I.R., to whom responsibility for the work has recently been transferred.

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Discussion.

The President: There is a time for second thoughts and remedial measures. That is a natural and inescapable conclusion in all branches of science. Sir James Jeans stated that the history of science can be divided into three periods—animistic, mechanical, and mathematical. In the study of friction we have most certainly passed that stage which arises simply from evidence of the senses. Now we are in the mechanical stage. Some of the more venturesome are on the fringe of the mathematical.

Students of lubrication are well aware of the observations of Faraday, Rayleigh, and Hardy. More recently they have turned their attention to Bowden and his associates. No discourse on friction would be complete without some reference to the stick–slip theory. A great deal of valuable work has been conducted upon this principle, and there is no doubt that it has been a great contribution to the study of friction and lubrication.

Frewing attempted to define a close correlation between stick–slip transition temperature and the degree of saturation of the adsorbed boundary film, the transition temperature being that temperature at which an adsorbed film of lubricant ceases to permit steady sliding and gives rise to stick–slip, or a change from an orientated film to some other re-arrangement.

Bristow designed an apparatus to enable him to study the subject in his own way. He came to the conclusion that stick–slip is not quite as Bowden had suggested. In fact, he went farther and expressed his belief that stick–slip is due to an instrumental phenomenon. In other words, it is a function of velocity and temperature.

Barwell and Milne have used the Bristow apparatus to carry the subject a stage farther. How far they have convinced their audience this evening we shall now learn. But whatever is said in the discussion, we shall still maintain that results are not obtained by rubbing a lamp, but by mechanism of some kind.

Until we can examine the structure of surfaces and films we shall be compelled to use indirect methods. Some technique is necessary to examine layers on solids. So far we have had to be content with the study of films on water. Electron bombardment has, of course, been used by Finch. But are we sure that high-speed electrons do not affect the configuration? Perhaps slow-speed electrons would be better, or perhaps a shorter exposure period. The electron microscope is now being used. Evidently everything depends upon technique.

The point which has been emphasized particularly this evening is the way in which the friction is measured; that particular point, I think, is the real keynote of the paper. I should like now to hear what some of our learned friends may have to say on this very abstruse subject.

DR BARWELL: Your remarks, Mr President, rather encourage me to think that others will have to take a bolder view than we took when preparing the paper. We took the view that we were speaking to people in the oil industry who were concerned principally with measuring this very elusive property. We have certain ideas ourselves on the basis of the mechanism, but we have not discussed them in the paper because we feel we ought to do one thing at a time; and as we understand the question of specification is becoming acute, we feel we ought to look to see how far experimental technique is available which will lead to a specification. I am very glad that we have taken that view, because the N.P.L. has been working on measuring friction for a good many years and we had tended to favour a certain standardized procedure. We were beginning to fall into the habit of generalizing too much on the results obtained from that standardized procedure. We, therefore, decided to find out whether alteration of conditions would lead to a different picture. As the results in the paper show, friction results are markedly affected by such factors as surface finish and temperature. I do not think we should be discouraged, however, because if data are gained methodically so that they can be analysed subsequently, the more data that are gained, the more likely are we to reach an understanding of the fundamental factors involved. On the other hand, if experiments are not made methodically, confusion will result.

Perhaps we owe you an apology for having presented what is in effect an incomplete piece of work. But we feel it is better to discuss work at stages during its progress than to wait until the investigator has finished his work and thinks he knows all about the subject; then his audience has to disillusion him, as inevitably it does.

We are hoping, therefore, to hear the views of people in the industry, first of all about their desire for a specification, secondly, about the sort of conditions their specification would have to meet, and thirdly, how much experimental trouble they are prepared to go to in the actual tests which a specification would require.

THE PRESIDENT: Dr Barwell has imposed an obligation upon us by his closing remarks, by asking us to assist him in suggesting a programme. Perhaps it will suit the convenience of speakers if we can deal with that as the discussion proceeds. I had hoped we should have had the opportunity this evening of hearing Dr Bowden; he was specifically invited, but unfortunately was unable to come. But he has sent a team here from Cambridge, and I feel sure that at least one of them would like to speak.

I think we should pay a compliment to Cambridge, because so much of this class of work has been done there.

MR K. V. SHOOTER: The only point I have to raise concerns the carbide results. At Cambridge we have been doing some work on four different types of carbide, differing in composition and in structure. All four give the same coefficients of friction, both for dry friction and when lubricated with cetane or with a cetane solution of lauric acid. The results are the same as those given by the authors of the paper. Can they give me any information on the composition and structure of the carbides they used?

MR MILNE: The carbide we used for these tests contained 9 per cent cobalt.

MR SHOOTER: No titanium carbide or tantalum carbide?

MR MILNE: No.

DR D. CLAYTON: It may be of interest to the meeting if I outline a little of the history of the early part of the investigation—prior to that dealt with in the paper.

When I was with the Ministry of Supply during the war a number of problems arose in which we thought the coefficient of boundary friction would be of assistance in explaining something observed or suggesting what should be done to solve those particular problems. Quite a lot of work, therefore, was put into the hands of the N.P.L.—it was in Dr J. R. Bristow's time—to give us friction–velocity curves. We were realistic enough even in those days to appreciate that the conditions would affect the results quite seriously, so we asked for the coefficients of friction to be determined under as closely as possible the conditions of the particular mechanism, and everything was made comparative. In many cases the results were distinctly helpful. The amount of work became rather extensive and we arranged for the Tin Research Institute (Mr P. G. Forrester) to do similar work, but approaching the design of apparatus from their own point of view (they chose a three-point contact and rotational motion). In turn they tackled a number of problems and accumulated further values. In the interests of economy we thought we should try to put the results together and build up something better than either series alone would give. First we suggested that the two parties should get together and compare results to see whether the coefficients of friction obtained in one place for particular sets of conditions would be the same as in the other. The first results for a series of lubricants and rubbing materials showed some rather horrifying differences. The two groups did a lot of work to find out the causes. They quickly established that the machines gave the same results for identical surfaces and that it was the preparation of the surfaces that was critical. Considerable success attended these efforts, and at the time publication of a paper was first thought of, it looked as though it might be possible to present to the Institute a joint paper which would describe the experiments carried out and outline standard conditions for the measurement of coefficients of kinetic friction. That would have been the preliminary stage to the Standardization Committee asking one of its sub-committees to take up the question and to establish the method on a wider basis. But that has not quite come off. Many of the main variables have been examined, and agreement reached at many points, but it has not yet been possible to present a well authenticated case. Dr Barwell and Mr Milne have instead reviewed some of the many factors affecting friction and also the requirements for a specification.

The ultimate use of boundary friction values in specifications was an incentive throughout the early work: they were thought to be valuable for control, once standard conditions had been established; moreover, the behaviour under other conditions could readily be ascertained by comparison,

using an established technique. This paper shows up the difficulties, but the fundamental need remains.

The impossibility of comparing results obtained by different workers is a regrettable feature of present-day work on boundary lubrication. We are accumulating masses of information, and much of it we are not able to use beyond the particular purpose of the paper in which it appears. The comprehensive programme referred to in this paper should go far to remedy this position.

I feel the authors have emphasized in the early part of the paper the enormous differences that *can* be obtained, perhaps to shock us into realism, whereas in the later part of the paper, more constructively, they indicate how to avoid some of the worst variations. The complexity is great, and it is most important to approximate and to choose basic conditions so as to present a comprehensible picture, pending the evolving of a satisfactory theory; the spirit of this analysis is well expressed on page 472: "The essential requirement is that a standard method of interpolation should be adopted . . ." and in other remarks in the later pages.

Although limited aims were set for the original programme, we realized that an enormous amount of information valuable in itself would be obtained in the course of the work. The question of finish, for example, is obviously of importance. There are two aspects: the geometrical, on which useful information is given in the paper, and the physical metallurgical nature of the surface. There is evidence from the early work that the latter is of considerable significance, independently of roughness. Much more requires to be done, but a potential importance lies in the fact that we may have to choose our production methods for piston-rings, journals, crankshafts, etc., to give a particular physical state to the surfaces, and not merely a certain geometrical finish, in order to get good rubbing behaviour. This line of investigation may allow this to be done purposefully, not as a vague inference from practical behaviour.

You have referred, Mr President, to "stick–slip." I vote quite definitely for presentation of results as friction–velocity curves; indeed, I would say that the Bowden group of workers would have given us quite a lot more information in their recent papers if they had used this form instead of referring to "stick–slip." In many cases it is impossible to infer from "stick–slip" records what it is that has changed, whereas friction–velocity curves show, for example, whether the friction has risen only at the lowest speed or whether a major change of friction has occurred.

Finally, I would like to state that I agree very much with the authors in the opinions they have expressed.

Mr E. A. Smith: I have been delving in the field of friction for about fifteen years and have come to the conclusion that it is a quicksand. The more one struggles against the surrounding coefficients, the deeper does one sink into the quicksands, and I am now up to my armpits in coefficients. For that reason I welcome the plank which the authors of this paper have put out. Perhaps I may now be able to crawl out of the quicksands in which I have been floundering for all of these years.

I feel that the analytical approach adopted by the authors speaks for itself, and their paper calls for a great deal of reading and careful thought.

The first question I would like to ask them is whether they have tested camphor and Borneol. Camphor is rather a unique substance, and seems to offer an abnormally low coefficient of friction under kinetic boundary conditions.

Secondly, I would like to ask whether the friction values given in Fig. 4 and elsewhere are for one traverse of the sliding member over the base plate, or whether those values represent an average of several runs. I can well imagine that the values for the first run, or certainly during the initial period of the first run of the sliding member, would be substantially different from those for the rest of the run when using certain kinds of lubricants.

Again, in Fig. 4, they quote values for "graphite" lubrication, and I would like to ask exactly what they mean by this expression. In my limited experience, I find that one can obtain almost any coefficient of friction for graphite, according to: (*a*) its purity and (*b*) its particle size. They give a curve for a lubricant, such as copper oleate, which is a well-defined chemical substance, but graphite is often referred to without an adequate definition or specification. You can obtain figures from 0·05 up to 0·3 as you wish, by adding a little silica for the latter values. Indeed, the purity of the graphite used is all important when quoting friction values.

Those quoted in Fig. 4 for graphite seem to me to be 50 to 100 per cent higher than numerous values which I hold for other machines, where colloidal graphite has been examined. These testing machines seem to give coefficients of friction for a thin graphite film, quite close to one another, considering the varying testing conditions. One machine that comes to mind is that designed by Professor Thoma of Munich, in which he employed two small steel cylinders rotating against one another at different speeds. The axes of the cylinders were inclined to one another; that is to say, they did not operate in the parallel condition. I hold numerous friction values for thin, pure, graphite films, of which the following are typical:—

Deeley Machine — 0·06
Bowen–Leben Machine — 0·07
Modified Deleey Machine — 0·07
Thoma Machine — 0·07–0·08.

In view of the above figures, I feel that the value of 0·12 given in the paper is somewhat high, and perhaps unrepresentative of what can be achieved by this form of lubrication. The result may throw some light on the characteristics of the machine used, for this certainly is not in line with a large number of other tests.

I cannot help feeling that the more coefficients of friction with which we are presented, the more fogged we may become in assessing the lubricating efficiency. But I think in their paper the authors are approaching the subject, not only from the experimental point of view, but also from the statistical aspect, and in so doing they are performing a very useful service. It is so easy to produce coefficients of friction, but it is another matter to present those in a context which will not give rise to misunderstanding.

THE PRESIDENT: You said you were interested in camphor. Will you say briefly why you have that particular interest?

MR SMITH : Camphor was used on some small sheet-rolling mills for steel and brass sheet, and gave a value of about 0·03 to 0·04, whereas the corresponding value, under the same experimental conditions for a fatty oil was, I think, about twice that value. I have no explanation to offer for this result, but the fact remains that the value obtained was extremely low. I raise the matter only as a point of general interest, if only to add yet one more coefficient of friction to the thousands we already have.

DR BARWELL : Reference has been made by Dr Clayton to the history of some of this work. I do not really accept his contention that the interest of the N.P.L. in kinetic friction dates from the time when Dr Clayton was at the Ministry of Supply, because Dr Clayton himself was interested in the subject long before he was associated with that Ministry. The interest goes back to the time of Sir Thomas Stanton. This paper does not attempt to give a complete bibliography of the workers in the field of kinetic friction; Dr Clayton will have gathered that, for his own name does not appear in the paper.

What he has said about our attempts to obtain correlation with the results of workers using a different type of machine is perfectly true, and I think the results we have heard this evening explain that completely.

That brings us to the point about what to do with the vast accumulation of data which Dr Clayton and Mr Smith have mentioned. We tried quite hard to put our own data into a form for presentation to such an Institute as this, because it should be of real service. But, like Mr Smith, we found ourselves more or less lost in a sea of data, and we came to the conclusion that from now on we would do our work on such a basis as a factorial experiment, so controlled that all the data would be of equal value. Thus we could make comparisons in future years and draw valid conclusions.

The physical nature of the surfaces, mentioned by Dr Clayton, has a marked effect on the coefficient of friction. Surfaces prepared by two different methods to the same average roughness as measured on the "Talysurf" instrument did give different results. It is easy to appreciate, perhaps, that the grinding operation, with its high local temperatures, can have a profound effect on the test results, an effect which cannot be simply accounted for by cold work. On the other hand, the machining operation can be an operation of cold work. In the tests described in the paper, we think that metallurgically the two surfaces are similar, and that only the surface finish varied.

I make the point about the factorial experiments because these experiments have been made with one material which is not normally regarded as a boundary lubricant. It was readily available, being an intermediate in the preparation of other substances which would be of greater practical interest.

Camphor has been mentioned by Mr Smith. Camphor, like graphite, is a substance which we can obtain in different forms and in different degrees of purity. We knew it was a traditional lubricant; people in workshops often used it to help them out of difficulties. In one experiment, in which we were working towards an industrial application, we tested a commercial grade of the material readily available and were disappointed by the results obtained with camphor. The coefficent of friction between steel and steel was as high as 0·4.

In regard to graphite, we, like Mr Smith, can give a very large range of coefficients of friction. I think that is quite understandable. One would expect a solid lubricant in discreet particles, such as graphite, to be affected very considerably by the factors of surface finish and roughness between surfaces. We have not figures as low as some of those of Professor Thoma, but we have had figures of 0·07. Savage,* of the General Electric Laboratories at Schenectady has shown the importance of water in effecting lubrication with graphite. In the study of graphite one must really follow some standardized procedure; otherwise the collection of data over a wide field, obtained under different conditions by different investigators, is bound to be confusing.

I want to emphasize that I do not feel it is a function of the apparatus. In the hands of a competent investigator forces can be measured with certainty, but the surrounding conditions may give rise to difficulties. We should regard the coefficient of friction as a ratio between two forces and then proceed to study the conditions which affect that ratio.

With regard to specification and to general study, we feel that a very great deal of information can be obtained by this experimental method, measuring friction. Whilst that method will not throw much light on the mechanism of boundary friction, it should enable us to check theories which are produced either as the result of speculation or from special experiments.

But another important factor, which has not been mentioned this evening, is the damage done to the surface, and it is our intention to pay equal attention to the microscopic and other examinations of the particular tracks, in addition to the coefficient of friction. That will not give quantitative information, but it may enable us to restrict the field of the various conditions which will help us not only to understand what is going on but also to justify restricting the range of a specification test.

Dr E. Tingle: To discuss the "stick–slip" question in the terms in which it has been posed is to flog a dead horse. There is, I believe, general agreement that intermittent "stick–slip" motion is dependant on a falling characteristic of the friction–velocity curve and that the frequency may depend upon the elastic constants of the measuring system. The question of what happens when the natural frequency of the measuring system is made very high is now being investigated in Cambridge by Dr Tabor.

Certainly much more has been read into the earlier tendency to consider "stick–slip" motion as a fundamental characteristic of sliding than was intended. However, it is worth pointing out that many combinations of metals possess a falling friction–velocity characteristic. As a result, since moving systems often possess a certain degree of elastic freedom, intermittent motion of the "stick–slip" type is of frequent occurrence in practice. In some cases, in fact, the elasticity of the surface irregularities might in themselves be sufficient to set up vibrations in the moving parts. Further, most workers agree that the type of sliding is profoundly affected by the nature of the surfaces and of any lubricant films that might be present. An analysis of the motion often gives valuable information about the mechanism of friction and about the nature and properties of the lubricant film.

* Savage. *J. appl. Phys.*, 1948, **19**, 1–10.

Coming to the question of the effect of surface finish on the coefficient of friction, I myself did a little work on this problem using copper lubricated by a solution of stearic acid in white oil. My results agree with those of Dr Barwell and Mr Milne that the roughness of the surface does not affect the value of the coefficient of friction very much. There was a small change, I found, but it was not very much greater than the experimental error.

One thing which was very surprising, however, was that when the surface was polished metallographically with production of a Beilby layer there was quite a large difference in the coefficient of friction. The value of the coefficient of friction for an abraded surface, for which a medium-grade abrasive paper was used, was about 0·1. With the same experimental conditions, however, the coefficient of friction on the metallographically polished surface was very much higher; I obtained coefficients of friction varying from 0·7 to 1.

Further, with regard to formulating a specification, the authors mention that to produce a standard surface finish for friction measurements, lapping might be an acceptable method. That was one of the standard methods we used. When emery powder was used on a lead lap, the friction results were low and variable. I found, for instance, that the coefficient of friction when steel slid on steel, when the lower test surface had been lapped with a lead lap, was about 0·2 to 0·3. If, on the other hand, the steel was prepared on abrasive paper the coefficient of friction was consistent at about 0·6. It was shown by microchemical analysis, that when the lead lap was used, lead was deposited from the lap on to the steel test surface. The low friction is then produced by the familiar thin-metallic-film-bearing action of the soft lead on the hard steel substrate.

Dr Barwell: We used a cast-iron lap, so that there is no risk of contamination with lead in the results given in the paper. If you consider the figures in Table I, showing the "Talysurf" and "Guild" Optical finish records, you will find that the reproducibility of surface finish is as reasonable as one might expect for such a tricky operation.

The reference made by Dr Tingle to the condition of the surface raises a very important point. If you think for a moment about the realities underlying these things you will realize that we are really concerned to a very large degree with the oxide layers covering the metals rather than the metals themselves. From the experiments of Vernon, Wormwell, and Nurse * it is quite clear in some cases that in the finishing processes we can alter the composition of the oxide layer. For example, when stainless steel is highly polished, there is chromium enrichment of the oxide film; so that there is a different oxide layer, having more chromium in it than that formed after, say, a machining operation. I think Dr Tingle and ourselves are agreed that the different nature of that oxide layer is so important that it can mask the effects of surface finish in certain cases. I think we disagree on the point as to whether it is a mechanical or a chemical effect. We have suggested that this hard, chromium-enriched layer provides high friction and surface damage with stainless steel by providing a hard abrasive which digs into the surface. I think Dr Tingle puts forward the view that the action of some of the good boundary lubricants is a chemical action, and

* Vernon, Wormwell, Nurse. *J. Iron & Steel Inst.*, 1944, 81.

requires the presence of an oxide and water for the reaction with the metallic surface to take place and that in stainless steel this hard chromium-oxide layer prevents any contact between boundary lubricant and basic metal.

DR TINGLE: I do not altogether like your interpretation of my interpretation. I do not think the effect of the chromic-oxide layer on stainless steel is due solely to its chemical characteristics; more probably it is due to its physical nature. I believe its physical nature is such that it forms an impenetrable barrier into which the fatty acids cannot penetrate and react. There is a considerable body of work which shows that, in order to achieve efficient boundary lubrication with a fatty acid, the layer of soap which is formed by chemical reaction must be of more than one molecular layer. If the oxide is porous, the reaction can take place and one can get the multi-molecular layer of soap. The chromic-oxide film on stainless steel, the oxide layer on aluminium, and probably also that on nickel, is compact and impenetrable. The acid may react to give a mono-molecular layer of soap, but not to give the multi-molecular layer necessary for really effective lubrication.

DR H. R. MILLS: It would help in the interpretation of these various curves if we knew a little more about how reproducible they are. I think Mr Milne quoted a figure of 5 to 10 per cent. That is based on experiments carried out with the same slider and lower surface and repeating fairly soon afterwards. If at a later date you prepared another slider of the same material and used what you thought was the same oil, would you get the same range of discrepancy between the curves?

There is another matter about which I am not certain—and I think that perhaps this has a bearing on the question of gear lubrication. I am not sure in which directions the surfaces have been finished. They are finished by lapping. Does not that leave the scratch marks and grooves in the direction of sliding on both surfaces, or is it in the direction of sliding on the lower surface and circumferentially on the upper surface? I mention this because, in a gear, the direction of finish is usually across the direction of motion on both surfaces. We have made experiments at the Motor Industry Research Association with two rollers moving together, with their edges in contact and the two surfaces moving at different velocities, so that there is a combination of rolling and sliding. With the finish marks round the circumference so that the grooves are in the direction of motion, the coefficient of friction is very much higher than if the finish is across the direction of motion. I do not know the reason; but it has been suggested that when the grooves are across the direction of motion their sides may possibly form a series of small wedges which may induce some measure of hydrodynamic lubrication. I should like the authors' views on that.

MR E. A. SMITH: Perhaps I may interpose a remark to Dr Mills regarding his observations on finishes. I have in my possession a report, which has not yet been published fully by my company, concerning the effect of finish-mark direction on wear. It was found that when the finish marks were parallel with one another on opposite rubbing faces, there was exces-

sive wear. When, however, the marks lay across one another, to give a kind of sawing action, wear was at a minimum. Quantitative data on this matter is available which I hope may be published later. (Some data are given in *Engineering*, 28.5.48, p. 506, Fig. 5.)

MR J. G. WITHERS: What practical significance do the authors place on boundary friction as applied to ordinary liquid lubricants when lubricating practical pieces of equipment such as engines and gear-boxes? In such equipment the losses will be due very largely to viscous friction, and the effect of changes of boundary coefficients of friction may well be negligible. Film strength and wear characteristics under boundary conditions would be relatively much more important.

MR J. F. T. BLOTT: Dr Barwell mentioned that he did not expect the radius of curvature of the slider to affect the coefficient of friction, but that he found that it did. Is it not difficult to ensure that you are not introducing another factor when changing the radius of curvature?

DR BARWELL: Dr Mills raises a very important factor when he refers to the direction of the surface finish. In our experiments the specimens were lapped in a random fashion to give a surface which, as will be seen by reference to Table I, has no directional properties. Previous friction experiments, including some by Dr Bristow while at the N.P.L., and certain unpublished results relating to scuffing and to slow wear, have shown us that directional properties of the surface may be of considerable importance. Whilst the results were in many cases conflicting for ground and machined surfaces, the cross-ridge condition, in several instances, gave better results than the parallel condition.

The scatter figures of 5 to 10 per cent quoted by Dr Mills refer to independent tests using freshly prepared surfaces on different specimens and a new sample of lubricant. Immediate repeat tests on the same specimens gave better reproducibility. This leads us to believe that some at least of the scatter may be due to the difficulty of providing identical surfaces on similar specimens and to lack of homogeneity in the material itself. Replication of tests in the manner described in the paper ensures that real differences between conditions of test are obtained and increases confidence in the mean values quoted.

Mr Smith has asked whether the results quoted were for one traverse of the slider over the plate or whether they represent an average of several runs. The figures quoted represent the mean of four determinations, but determinations on freshly prepared surfaces. The question of "running-in," like that of direction of surface finish, is important and provides considerable scope for investigation. In the present series of tests the number of factors was already so large that it was decided to leave these two other factors for investigation at a later date. Accordingly, the determinations were deliberately made on fresh and non-directional surfaces.

Mr Blott has mentioned the possibility of changing other factors also when changing the radius of curvature. If Hertzian conditions of contact are assumed to apply, then the pressures between the contacts will be affected by changes in either the radius of curvature or the applied load. The interaction between these two factors is still being studied, and it may

be that some other criterion such as, say, the mean contact pressure, is the important factor involved.

As to the practical significance of these results we had rather hoped that we should be told something about that this evening. As research workers we try to be practical and we also try to be analytical. We are conscious that in a great many cases the real problems occur with mixed lubrication. To work with a mixture is difficult unless you know the ingredients. I think we can say that we know the hydrodynamic ingredients; and this work is an attempt to study the other ingredients. Mr Milne is working on another experiment in which the ingredients are mixed together; we shall know our mixture very much better if we know the particular ingredients.

In conclusion, I would like to say that this work represents an attempt to study one of the most difficult aspects of the subject, and I am afraid some years will elapse before we can attempt to present a paper in which we can claim complete assuredness about our knowledge of the subject.

Inasmuch as the President has referred to the N.P.L., I would say that this is probably the last paper you will have on this subject from the N.P.L., because the lubrication section of the engineering research work there is being transferred to the new establishment which has been set up in Scotland, where increased facilities will be provided under the new Mechanical Engineering Research Organization of the Department of Scientific and Industrial Research. We shall endeavour to carry on the traditions of the N.P.L. in the new establishment.

Vote of Thanks.

The President: We are very grateful indeed to Dr Barwell and Mr Milne for their contribution to the study of friction. They have exhibited great patience and a devotion to science, and they worthily subscribe to the thought that, notwithstanding the very able brains and the picturesque work which has been applied to the elucidation of friction, it still remains obscure. They have carried forward the torch of knowledge. Whatever they may have discovered, there will always be fashions in science, as in everything else.

The hope was expressed by Dr Barwell that we should be able to tell him a little more about the practical applications. I do not think we need be too fussy about the practical applications at this stage. The research worker has to put forward the fundamental consideration; we are a long way from being able to marry the academic aspect and the practical applications, and we have simply to be patient. But the two are slowly merging, and eventually we shall be able to see exactly where they meet; then industry can take full advantage of this noble work which has been going on at Cambridge, the N.P.L., and elsewhere. We are very grateful indeed to the authors of the paper for having given us the benefit of their work, perhaps for the last time from the N.P.L.; we feel sure that from the Scottish air they will derive renewed vigour and will come back to tell us a lot more.

(The vote of thanks was heartily accorded, and the meeting closed.)

AN IGNITION DELAY METER FOR THE DETERMINATION OF CETANE NUMBER.

By H. J. Hulf,* A. Rubach,* and J. G. Withers * (Associate Member).

Summary.

The instrumentation standardized for use with the A.S.T.M. fixed-delay method of Cetane No. determination has not been found entirely satisfactory in use. On this account an alternative was sought which would be more accurate and yet sufficiently simple and reliable to be handled by relatively unskilled operators.

In the new instrument described in this paper commencement of injection and combustion are detected by utilizing the modified output wave forms of two electro-magnetic pick-up units; and pulse techniques enable a meter reading of ignition delay to be obtained in terms of crankshaft degrees. Injection advance is observed similarly. The calibration is unaffected by variations in engine speed; and the ignition delay can be measured even under accelerating conditions.

The prototype instrument gave an accuracy of $\pm\frac{1}{4}°$ and a discrimination of $\pm\frac{1}{16}°$; and the scatter of readings in Cetane No. determinations was roughly halved, and the speed of operation doubled by its use.

It is concluded that the instrument is a satisfactory solution to the instrumentation problem of Cetane No. determination.

Introduction.

The A.S.T.M. method of Cetane No. determination [1] involves adjusting the injection timing and compression ratio of the C.F.R. diesel engine, running under standard conditions, so that injection occurs 13° before top dead centre and combustion occurs at top dead centre. This fixed ignition delay of 13° is obtained for any fuel by a suitable adjustment of compression ratio; and the Cetane No. of a sample fuel is determined by interpolation between the compression ratios found for a five Cetane No. bracket of reference fuels.

Injection is detected by arranging that the motion of the spray valve closes a pair of electrical contacts and thereby flashes a discharge lamp mounted on the flywheel.

Combustion is detected by a bouncing pin, so adjusted that the contacts just fail to close on compression pressure alone. The increase of pressure due to combustion closes the contacts and flashes a second discharge lamp mounted on the flywheel. The lamps are so disposed that when injection and combustion occur at the correct times the respective flashes coincide with a cross-wire.

Some defects of this arrangement are :—

(*a*) The contacts wear and require frequent cleaning and dressing because of contamination and pitting.

(*b*) The contact spring tensions require very accurate adjustment if the system is to work at all, and this necessitates frequent re-adjustment to compensate for wear and temperature effects.

* Anglo-Iranian Oil Co. Ltd.

(*c*) Since the contacts must be open initially, the indications are in error by the time taken for the gap to close. Tests in which an electromagnetic pick-up was used to detect injection have shown that the contact method of indication may lag as much as 2°.

(*d*) The method imposes considerable optical strain on an operator engaged in routine testing.

These defects are almost entirely due to the use of electrical contacts, and a method of presentation which is not remote indicating.

Optical or cathode-ray oscillographs may be used to study the mechanical movements of a spray valve and the deflection of a diaphragm subjected to the combustion pressure, but the resulting diagrams can be interpreted correctly only by an experienced operator; and, although these instruments probably represent the present limits in engine-indicator practice, they are best regarded as research tools. In addition, unless comparatively complex time-bases are provided, the angular scale of the diagram is sensitive not only to engine speed variations, but also to variations in the angular velocity of an engine crankshaft running at constant mean speed. The latter effect can be particularly troublesome in the case of a single-cylinder four-stroke engine such as the C.F.R. diesel.

The instrument described in this paper is based on the need to overcome the forementioned difficulties and limitations and the following specification of performance was set as the minimum requirement :—

(*a*) The angle between injection and combustion and the angle between injection and top-centre must be measured with an accuracy of better than $\pm \frac{1}{4}°$, at all normal diesel-engine operating speeds.

(*b*) The measurements must be capable of remote and stable indication, preferably on an open-scale meter, and they must be unaffected by engine speed.

(*c*) It must be possible to recalibrate by some quick and simple means while the instrument is on the engine.

(*d*) To give speed of operation and reliability of results, no controls should be provided other than a switch for selecting the measurement to be made and a single pre-set control for recalibration.

(*e*) The operator must not be required to exercise any interpretative skill and as far as possible should be prevented from doing so.

The Measurement of Angular Intervals.

In many engine measurements the parameter of interest is not time but the crankshaft angle separating cyclically recurrent events. A typical case is found in the indication of spark advance in spark-ignition engines.

A satisfactory spark-advance indicator had already been developed at the Sunbury laboratory of the Anglo-Iranian Oil Company. In this instrument short-duration pulses were derived from the spark and from a reference point on the flywheel, and these were applied in the form of trigger pulses to a high-speed electronic switching circuit which developed a train of rectangular waves; the mark–space ratio of the train was proportional to spark advance and could be read on a moving-coil meter.

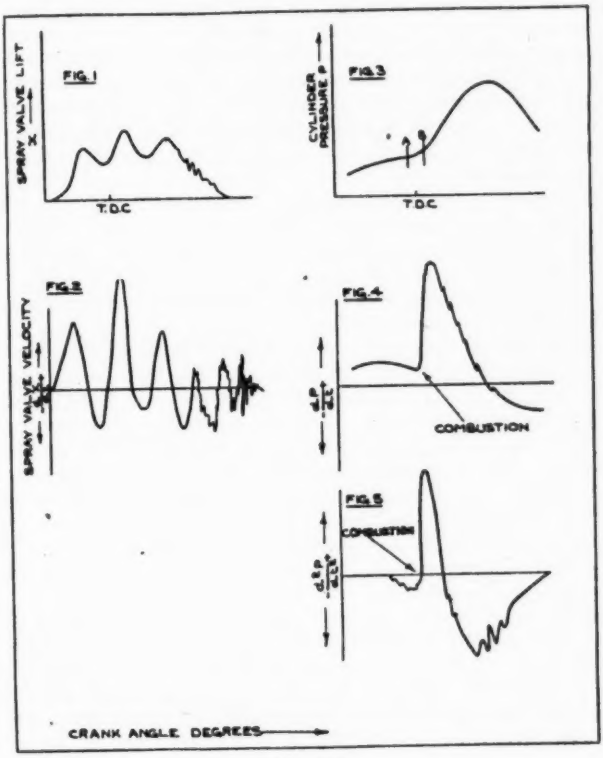
The Ignition Delay Meter makes use of the same principle, and short-

duration pulses are derived from the output waveforms of pick-ups associated with the spray valve and combustion chamber respectively.

Pick-up Units.

Detection of Injection.

Various methods have been used successfully for the detection of commencement of injection. Of the more practical may be mentioned those



Figs. 1–5.

THE DETECTION OF INJECTION AND COMBUSTION.

making use of capacity changes, those employing photo-electric cells, and those employing electro-magnetic units.

The motion of the spray-valve needle (Fig. 1) does not normally exhibit a sharply defined commencement, and the velocity diagram (Fig. 2) is much better in this respect. Electro-magnetic units have, for this application, the advantage that their output is proportional to velocity, and thus they avoid the need for differentiation; they have the further advantages of reasonably high sensitivity, robustness, and easy application. As a result

of these considerations an electro-magnetic pick-up unit of the type used in the Standard-Sunbury engine indicator [2] has been adopted for detecting commencement of injection in the Ignition Delay Meter. The output of the pick-up, as will be seen later, is amplified and then applied to a pulse generator.

Detection of Combustion.

The processes of ignition are accompanied by intense ionization and luminescence. The region of ionization which accompanies the flame front may be detected by the insertion of a voltage probe into the combustion chamber, but the indication given is somewhat late; the degree of lag depends on the point in the combustion chamber at which the nearest ignition commences, and this point varies from cycle to cycle. Thus the ionization method tends to indicate an erratic commencement of ignition which lags behind the combustion-pressure rise by an amount which experiment has shown to be as much as 1·5°.

The production of flame and radiation accompanying ignition may be detected by a suitably placed photo-electric cell, but earlier studies have shown that the production of visible radiation occurs after ionization, and thus an even later indication of ignition is given by this method. There would also be considerable maintenance difficulty in preserving a clean surface inside the observation window.

The most promising approach is offered by utilizing the rise in pressure which accompanies combustion. Reference to Fig. 3 shows that combustion starts in the region AB, although the precise point is ill-defined and for some fuels is almost indiscernible. The first derivative of the pressure diagram shown in Fig. 4 offers a far more accurate indication of commencement of combustion. But the point of contraflexure is not uniquely defined in terms of amplitude, and it is difficult to derive a short-duration pulse directly from it. By taking the second derivative (Fig. 5) the combustión point is seen to be that point in the waveform at which the first positive-going excursion occurs; and, by applying this waveform to a pulse generator, the necessary pulse can be obtained.

The ignition-delay meter employs a variable-reluctance type of electromagnetic pressure pick-up with a diaphragm exposed to the combustion-chamber pressure. This is identical with that used in the Standard-Sunbury engine indicator.[2] The output of the pick-up is proportional to the rate of change of pressure, and the second derivative is obtained by electrical differentiation.

Practical Electronic Circuits.

The circuits illustrated in Figs. 6 and 7 have been developed along the lines indicated above.

Ignition Delay.

The output waveform of the injection pick-up is amplified in valves V4 and V5 (Fig. 7) and then applied to the grid of V6, a gas tetrode. The first positive-going portion of the waveform causes this valve to conduct, discharging the anode condenser, which then slowly recharges to H.T. voltage

(Fig. 10). During the very short time interval that V6 conducts, a positive pulse of about 10 micro-seconds duration is produced at the cathode (Fig. 11), which is then applied to trigger one side of the electronic switch, which is made up of valves V7, 8, 9, and 10.

The combustion pick-up output waveform is used similarly to trigger V3, after it has been amplified in V1 and differentiated in the short time-constant coupling to V2.

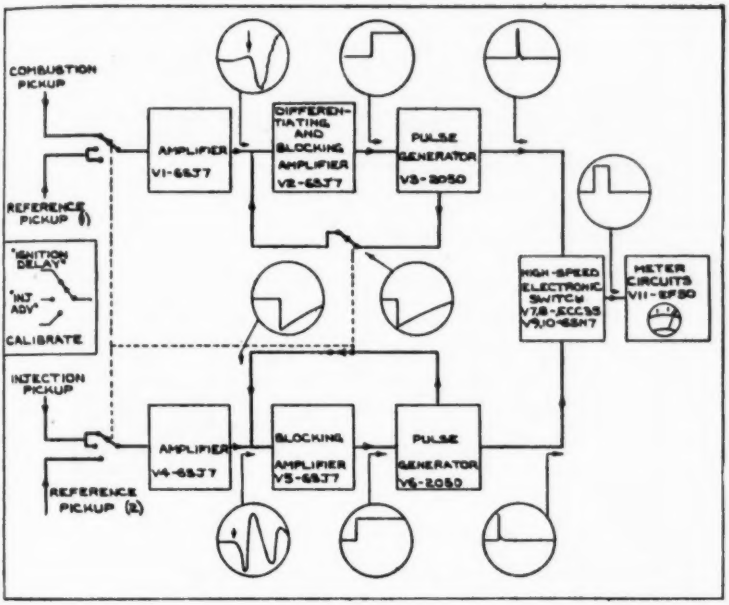


FIG. 6.

FUNCTIONAL SCHEMATIC.

After their commencement both injection and combustion waveforms make many positive-going excursions. It is therefore necessary to block all those parts of the waveform except the earliest, otherwise the electronic switch will be triggered many times during the period of one waveform, giving spurious effects. This is done by feeding back the long-duration pulses at the anodes of V3 and V6 to suitable points in their respective channel amplifiers (Figs. 9 and 14).

The electronic switch is of the type in which the voltage relationships may be in one of two states of equilibrium, both of which are stable. The arrival of the injection pulse causes the voltage at the anode of V10 to assume its upper stable value, and the arrival of the combustion pulse causes it to revert to its lower stable value. The transition from one state to the other takes about 2 micro-seconds, and this particular circuit has been tested at switching rates up to 110,000 per sec. The cyclical repetition of this pro-

cess results in the generation of a train of rectangular waves (Fig. 17), the mark–space ratio of which is directly proportional to the angular interval between injection and combustion. The rectangular waveform is coupled to a pentode which is normally cut-off, conduction occurring only during the interval between injection and combustion. The resulting pulses of anode current are smoothed by the anode capacity to a mean value indicated by the moving-coil meter.

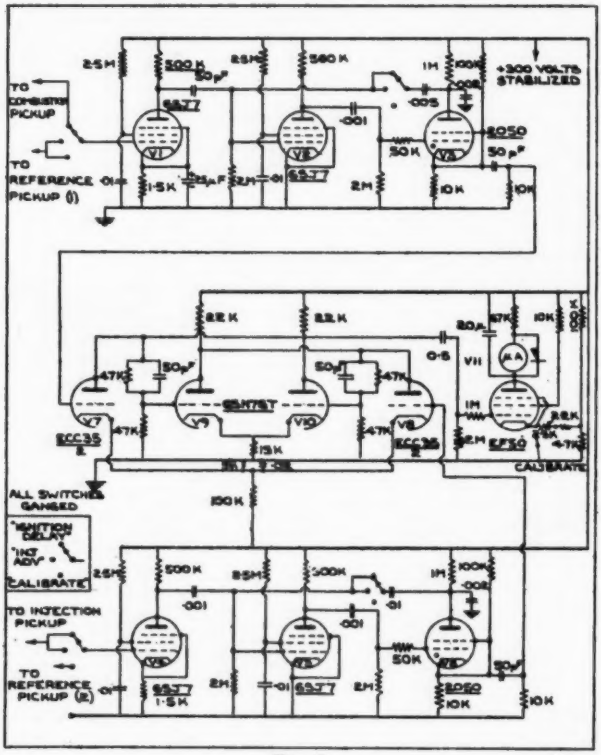


FIG. 7.

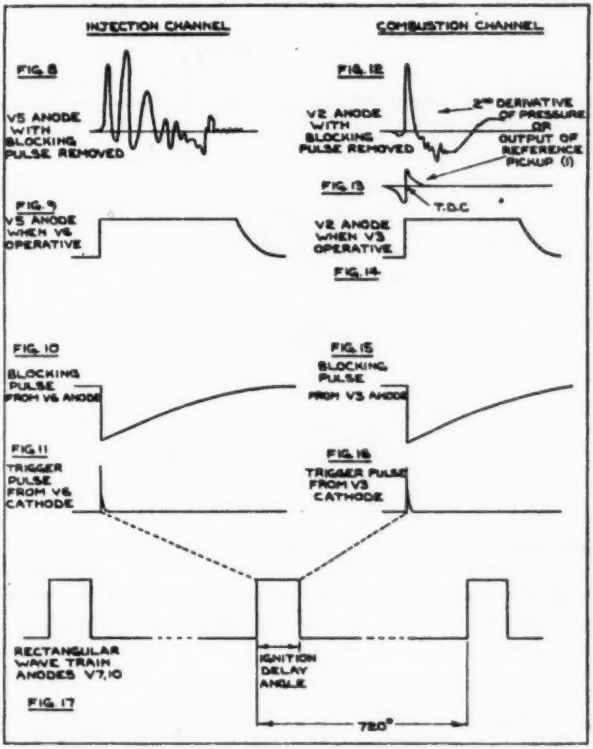
CIRCUIT SCHEMATIC.

In order that the mean value indicated by the meter shall be proportional to the mark–space ratio only, and not to the recurrence frequency as well, it is essential that the charge and discharge time-constants of the anode circuit shall be equal. This will only be so if the internal impedance of V11 is very much higher than the load resistance. The internal impedance of V11 has therefore been increased by the application of negative current feedback.

The meter is shunted by a rectifier to protect the movement against surges which may occur under fault conditions.

Injection Advance.

Injection advance is measured in relation to a reference point on the flywheel provided by a chisel-edged projection passing near a fixed electro-magnetic pick-up. The projection coincides with the pick-up at top dead centre, and this point in the equivalent waveform (Fig. 13) triggers V3 to provide an actuating pulse for the electronic switch.



FIGS. 8–17.

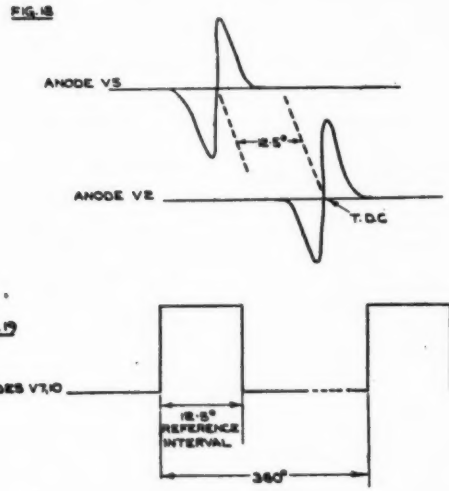
"IGNITION DELAY" AND "IGNITION ADVANCE" WAVEFORMS.

Calibration.

A further electro-magnetic pick-up is mounted such that the projection of the flywheel coincides with it at, say, 12½° before top dead centre. The waveforms from the two flywheel pick-ups (Fig. 18) situated 12½° apart are amplified and used to trigger the electronic switch in the manner as previously described.

The calibration square wave (Fig. 19) occurs every revolution, while the delay and injection square waves recur every two revolutions in the case of a four-stroke engine. Thus the standard calibrating-meter deflection is

double, and in the case considered is equivalent to 25°. The meter deflection is then adjusted to read full scale by varying the anode current through V11.



FIGS. 18–19.
"CALIBRATE" WAVEFORMS.

PERFORMANCE TESTS.

The prototype instrument (Fig. 20) has been applied to an A.S.T.M. C.F.R. diesel engine. The pressure pick-up was fitted in the bouncing-pin hole by means of an adaptor so arranged that there was no indicator passage and the diaphragm was subjected directly to the pre-combustion chamber

TABLE I

Sample.	A.S.T.M. result, Cetane No.	Difference meter A.S.T.M. Cetane No.
1	53·1	−1·9
2	69·0	−0·2
3	53·0	+1·3
4	51·8	−0·4
5	28·0	0
6	45·0	−1·3
7	57·2	+2·2
8	47·2	+0·8
9	38·2	+1·8
10	41·6	+1·8
11	52·1	−0·4
12	57·5	−0·7
13	52·6	−0·4
	Mean algebraic difference = 0·1	

FIG. 20.

[*To face p.* 492.

DEVIATION
20
0
-20
0
DEVIATION
40
20
0
-20
-40

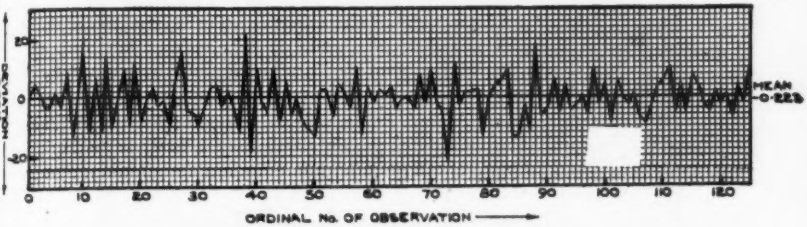
pressure. The injector was modified so that a mild-steel extension of the needle-spring cap was brought near to the pole piece of the injection pick-up.

The trigger pulses obtained were found to agree very closely with the points selected visually on a cathode-ray oscillograph trace.

A number of tests were made to compare the Cetane No. obtainable with the new ignition-delay meter with those previously obtained using the standard instrumentation. Three readings were taken for each of the

FIG. 21.

DELAY METER. SCATTER OBTAINED BY SUBTRACTING (N + 1)TH FROM NTH MICROMETER SETTING IN ORDER. STANDARD DEVIATION : 0·0082″ = 0·83 OCTANE NO.



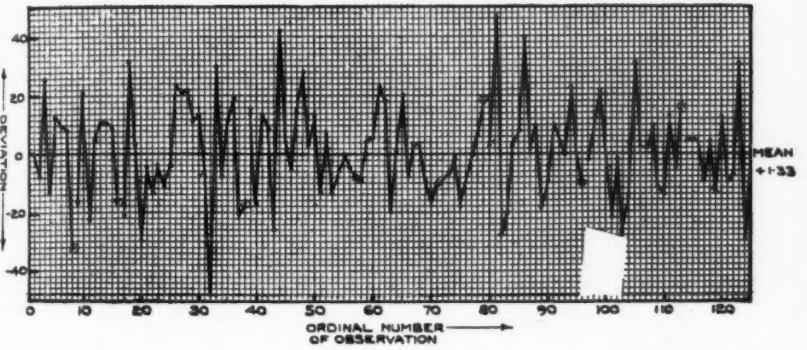


FIG. 22.

A.S.T.M. INSTRUMENTATION SCATTER OBTAINED BY SUBTRACTING (N + 1)TH FROM NTH MICROMETER SETTING IN ORDER. STANDARD DEVIATION: 0·0172″ = 1·7 OCTANE NO.

reference-fuel blends and the sample fuel in both cases. The results obtained are given in Table I; they show no greater deviation than the normal experimental error of the standard instrumentation, and there is no evidence that the ignition-delay meter treats fuels selectively.

Assessment of the relative errors introduced by the two instruments was approached in the following way. A large number of readings of the compression ratio required to give the standard delay angle of 13° was taken using the same fuel throughout (No. 12, 57·5 Cetane No.). As the readings involved operation during several hours, the effects of engine drift were reduced by subtracting each reading from the preceding one. The scatter diagrams thus obtained for both methods are given in Figs. 21 and 22. The

relative merits of the two systems are readily discernible from these diagrams and also from the histograms of Fig. 23.

The deviations in terms of compression-micrometer setting were converted into terms of Cetane No. by determining the guide-curve sensitivity between 55 and 60 Cetane No. A hundred readings of the micrometer setting for 55 cetane and a further hundred for 60 cetane were used to obtain the mean change for a 5 Cetane No. bracket in this region. The figure obtained was 0·010 inches per Cetane No. The standard deviation using the A.S.T.M. instrumentation is then 1·7 Cetane Nos., whilst that of the ignition

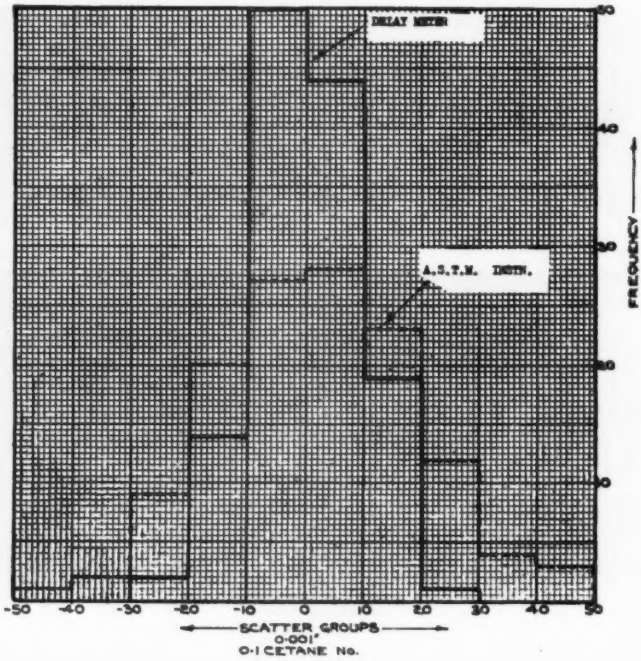


FIG. 23.

DELAY METER AND A.S.T.M. INSTRUMENTATION HISTOGRAMS.

delay meter is 0·8 Cetane No. The corresponding 95 per cent probability error values are 3·3 and 1·6 Cetane No. respectively.

These results indicate that the ignition-delay meter has an accuracy of approximately twice that of the A.S.T.M. method; it was found also that the results could be obtained in about half the time with the former.

The ultimate accuracy of the ignition-delay meter is bound up with the scale discrimination of the moving-coil meter. The meter used had a 4-in dial and a full-scale reading of 25°. With this the accuracy was $\pm \frac{1}{4}°$, and the engine conditions could be reset to $\pm \frac{1}{10}°$ with ease. These results were confirmed by comparison with the Standard-Sunbury engine indicator.

Discussion.

The terms of the specification have been met successfully and in part improved upon :—

(*a*) An accuracy of $\pm \frac{1}{4}°$ is possible, and a variation of $\frac{1}{10}°$ is readily noticeable.

(*b*) The delay meter may be situated at any convenient operating point and is unaffected by variations in lead length.

(*c*) The full-scale reading can be recalibrated whenever desired by the operation of a switch and the adjustment of a pre-set control to give full-scale deflection.

(*d*) The only operational control is a selector switch.

(*e*) The electro-magnetic pick-ups are extremely robust and, from previous experience, are capable of thousands of hours of trouble-free service. The diaphragm requires decarbonizing occasionally, but not more frequently than the engine.

(*f*) For Cetane No. determination by the fixed-delay method, a single mark on the meter at 13° is all that is necessary.

(*g*) Engine troubles encountered during the work were a need for a top overhaul and a faulty and carbonized spray valve. The first was apparent from the erratic nature of the ignition-delay interval and the second from the unsteadiness of the injection-advance reading.

Conclusion.

An instrument has been developed possessing considerable advantages over previous methods; and, owing to its stability and ease of operation, it is particularly suitable for Cetane No. determination.

Acknowledgment.

The authors wish to thank the chairman of the Anglo-Iranian Oil Company for permission to publish this paper, which has described work carried out at the Research Station at Sunbury-on-Thames.

References.

[1] "Tentative method of test for ignition quality of diesel fuels," A.S.T.M Designation D. 613–47T. "A.S.T.M. standards on petroleum products and lubricants," December 1946.

[2] "High speed engine indicators," by E. S. L. Beale and R. Stansfield. *The Engineer*, 26.2.37 and 5.3.37.

THE CORROSIVE SULPHUR TEST.

By G. Claxton (Associate Fellow)* and K. H. V. French.*

Summary.

By means of an addition to the copper-strip test it has been possible to study the corrosion of copper by motor fuels on a more quantitative basis than hitherto. This addition, which is described, depends upon conversion of the sulphide stain on the strip into hydrogen sulphide, which is estimated colorimetrically.

New tests have emphasized that corrosion due to elementary sulphur is not proportional to the quantity present, due to the effect of corrosion inhibitors. Corrosion by hydrogen sulphide is not affected by inhibitors to any great extent. The mutual activation of corrosion by hydrogen sulphide and elementary sulphur has again been studied on a quantitative basis. This phenomenon is important if fuels are to be blended, and in relation to storage. Contamination of stocks by hydrogen sulphide, for example, by bacterial reduction of sulphates in tank-water bottoms, may produce a greater effect than anticipated.

The inhibitor most commonly present in motor benzole and other benzole fractions appears to be a peroxide of either *cyclo*pentadiene or its dimer. The quantity of peroxide necessary to cause inhibition is extremely small and cannot be detected by the starch-iodide reaction. Its presence is inferred, however, from experiments in which the pure diolefin was added to non-inhibiting benzoles.

Introduction.

Owing to the number of copper and brass parts used in the construction of the fuel systems of petrol-driven cars, it has been customary for a considerable time to ensure that motor fuels do not contain sulphur compounds that may corrode these metals. Benzole fractions used for certain industrial purposes, particularly for the manufacture of printing inks for intaglio and rotagravure printing, must also be free from these impurities. Hydrogen sulphide and elementary sulphur are practically the only substances responsible for copper corrosion by petrols and benzoles. These substances may arise, or remain, during refining. A further source, in petrols, of elementary sulphur, is the use of the doctor process for removing mercaptans.

For many years various modifications of the so-called copper-strip test have been used for detecting and limiting corrosion by motor fuels. The principle of the test is to heat a strip of polished copper foil in a specified volume of the fuel at a stated temperature and for a stated period. Afterwards the strip is removed and observed visually. The origin of the test is obscure, although it was certainly known as far back as 1918.[1] In spite of the well-established character and proved usefulness of the test, difficulties have always existed with its interpretation and, although numerous papers have been published on the test, misconceptions still exist concerning its significance. These difficulties are all associated with the following facts :—

(1) Comparison of the corrosiveness of a sample depends on a written description of the appearance of copper strips produced under specified

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conditions by samples of varying degrees of corrosiveness. Precise description of the appearance of the strips is impossible.

(2) There is no quantitative relationship between the amount of copper sulphide produced and the quantity of hydrogen sulphide or elementary sulphur in the sample. This statement, which had frequently been made and as frequently overlooked, is particularly true of the corrosion produced by elementary sulphur, owing to the effect of certain corrosion inhibitors.[2, 3] Information concerning the exact nature of the mechanism of inhibitors is still very scanty.

(3) The same weight of copper sulphide, spread over the surface of a copper strip, will not invariably produce the same appearance. A further complication arises from the fact that hydrogen sulphide and elementary sulphur produce different sulphides.[4]

Several methods [5] have been devised for estimating the amount of corrosive sulphur in fuels, probably the best of which is that of Garner and Evans,[6] in which the fuel is refluxed with copper bronze, the sulphide produced being estimated gravimetrically. More recently Bolt [7] has described the preparation of permanent standards for comparative purposes when using the A.S.T.M. variation of the copper-strip test. These tests fail to give a true picture of the corrosiveness of a fuel for the reasons already stated.

A further step in carrying out the copper-strip test has now been devised in these laboratories. This modification, which has received a wide private circulation in the benzole industry, has not hitherto been published, but it will be included in the revised edition of "Standard methods for testing tar and its products" to be published shortly by The Standardization of Tar Products Tests Committee. The addition to the test has enabled some of the phenomena connected with corrosion, particularly that of corrosion inhibition, to be examined on a quantitative basis. These investigations are described below, but it seems desirable first to give a description of the modification to the test.

Experimental.

(a) *Modified Copper-strip Test.*

It has been shown that incipient corrosion of a copper strip under the conditions of the S.T.P.T.C. copper-strip test [8] occurs with about 0·01 mg per 100 ml of sulphur as hydrogen sulphide and with less than 0·1 mg per 100 ml of elementary sulphur. There is no reason to believe that the copper strip removes all the corrosive sulphur present, and it is clear that attempts to measure the corrosion by weighing the strip would require the use of very delicate balances and special technique. Conversion of the sulphide on the strip to hydrogen sulphide, by treatment with hydrochloric acid, therefore, seemed much more practicable.

Attempts to estimate the hydrogen sulphide produced in this way by the methylene-blue reaction or the sodium-nitroprusside reaction, were not satisfactory, but it was found possible to standardize a test based on the D.S.I.R. method for estimating toxic quantities of hydrogen sulphide in air.[9]

The method of carrying out the test is as follows : A stain is produced on

a polished strip of electrolytic copper 30 by 20 mm by treating it with 50 ml of the sample for 2 hr at 50° C, in the manner standardized by S.T.P.T.C. Briefly, this test requires a polished copper strip 30 × 40 mm to be heated in the sample at 50° C for 2 hr, the corrosiveness of the sample being judged by the appearance of the strip after treatment. The following additional test is then applied :—

Apparatus.

Streaming apparatus as shown (Fig. 1).
Aluminium paper-holder to expose a circular area ¾ in diameter.
Lovibond All Purposes Comparator.
Lovibond disc.

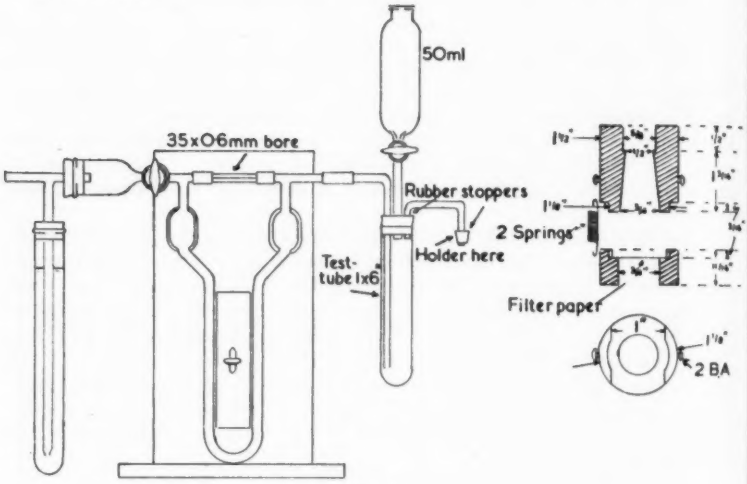

FIG. 1.
CORROSIVE SULPHUR TEST.

Reagents.

Pure Hydrogen. This gas shall not stain a lead-acetate paper when streamed through the apparatus for 30 min as described under method. Carbon dioxide, air, or nitrogen shall not be used.

Hydrochloric Acid. One part by volume of 36 per cent w/w acid diluted with one part by volume of distilled water. The diluted acid shall be tested for freedom from chlorine by further diluting 2 ml to 20 ml, and adding 1 ml of 10 per cent cadmium-iodide solution and 1 ml of starch solution. No blue colour shall be produced.

Lead-acetate Papers. These shall be prepared by soaking strips of Whatman's No. 1 filter-paper, 1 in × approximately 12 in, for 1 min, in a cold aqueous solution prepared by dissolving 10 g of lead acetate in 90 ml of distilled water and adding 5 ml of glacial acetic acid and 10 ml of pure glycerol to the solution. The superfluous liquid shall be allowed to drain off, and the papers shall be dried by hanging them over glass rods in a steam-

oven at 90° to 100° C, in an atmosphere free from hydrogen sulphide, until just dry (10 min). They shall then be cut into lengths of 2 in and shall be stored in a glass-stoppered, airtight container and be used within 14 days of preparation. The strips shall be handled by the corner so that the portion exposed in the aluminium holder does not become finger-marked.

Method.

The apparatus shall be assembled with 20 ml of the hydrochloric acid in the separating funnel, the copper strip in the test-tube, a paper strip securely held in the aluminium holder by joining the two halves together with the spring clips provided, and the holder in position at the end of the train. Hydrogen shall be streamed through the apparatus for 10 min at a rate of about 6 litres per hr. The flow-meter used for the oxidation test Serial No. L.B.10–38 * with a different capillary as shown is suitable for measuring the gas rate. At the end of this period the paper shall show no stain. The acid shall then be run into the apparatus, the tap on the separating funnel closed, and the gas stream continued for a further 30 min. At the end of this period the paper disc shall be changed quickly without stopping the flow of hydrogen. The first strip shall be allowed to dry for 1 min and shall then be placed on the right-hand side of the open back-flap of the Lovibond All Purposes Comparator. A clean blank of filter-paper shall be placed on the left-hand side of the Comparator. The apparatus shall be held about 18 in from the eye, so that the papers are illuminated evenly by a good north daylight and the disc shall be rotated until a match is obtained. If no match is possible, the next highest standard shall be taken. It is essential for accurate matching to use daylight as recommended. The second paper shall then be examined. If the streaming has been adequate, this paper will have remained unchanged, but if a slight stain is obtained after a further 30 min streaming, an approximate result may be obtained by adding the result for this paper to that of the first paper.

Reporting.

The sample of benzole shall be reported as causing a corrosion of the copper strip that will produce hydrogen sulphide equal to the number of micrograms (1 microgram $= 10^{-3}$ mg) of sulphur as hydrogen sulphide marked on the matching standard or as less than the next higher number.

Note.

The addition to the copper-strip test described above may be adapted to determine small quantities of hydrogen sulphide in benzole. For this purpose the apparatus shall be swept out as described and a convenient volume, say 10 or 20 ml, of the sample shall be run in from the separating funnel. The test shall then proceed as described, the result being calculated to give micrograms of sulphur as hydrogen sulphide in 100 ml of the sample. If the sample contains too much hydrogen sulphide for a match, pure benzole free from hydrogen sulphide shall be placed in the separating funnel and a small quantity of sample added to it from a burette that has sealed to it a

* S.T.P.T.C. "Standard methods for testing tar and its products, 1938, p. 155.

jet sufficiently long to enable it to be dipped below the surface while the sample is being run in.

Although it is advisable, when using this modification of the copper-strip test, to treat the stained strips with acid immediately they are produced, storage for up to two days is permissible and not likely to cause error, provided the strips are stored in closed containers. Beyond this time less hydrogen sulphide is evolved than from newly stained strips, due presumably to oxidation of the sulphide to sulphate. This was proved by treating twelve copper strips in twelve portions of the same benzole. The corroded strips were then removed, cut diagonally and paired alternately. Six pairs of half-strips were treated immediately in the streaming apparatus, and the remaining six pairs were stored for various periods in corked boiling-tubes before testing. The results of these tests are given in Table I.

TABLE I.

Effect of Storage on Stained Copper Strips.

Pair of half-strips.	Before storage.		Days of storage.	After storage.	
	Appearance.	mg × 10^{-3} S as H_2S evolved.		Appearance.	mg × 10^{-3} S as H_2S evolved.
1	Slight brown	3·5	1	Slight peacock	4·0
2	,, ,,			,, ,,	
3	Slight brown	2·0	2	Slight brown	2·5
4	,, ,,			,, peacock	
5	Brown, slight peacock at edges	4·5	3	Brown, peacock edges	2·0
6	Slight brown			,, ,,	
7	Brown edges	4·5	5	,, ,,	2·0
8	,, ,,			,, ,,	
9	Brown edges	4·0	6	,, ,,	1·5
10	Slight brown			,, ,,	
11	Slight brown	3·5	7	,, ,,	2·0
12	,, peacock			,, ,,	

(b) *The Effect of Hydrogen Sulphide on the Corrosion by Elementary Sulphur.*

It has already been mentioned that the sulphide produced by elementary sulphur differs from that produced by hydrogen sulphide. The appearances of the strips produced by these two substances also differ. Small quantities of elementary sulphur produce microscopic cones of blue-black sulphide at widely separated areas on the strip. Corrosion appears to be particularly prone to occur along the line of any minute scratches on the surface of the copper. In the initial stages of corrosion the cones of sulphide are difficult to see when viewed perpendicularly, but are generally noticeable if the strip is viewed obliquely. If the concentration of elementary sulphur is increased the area covered by sulphide increases, until the boundaries of the

sulphided areas meet and a uniformly black strip is produced. Hydrogen sulphide, however, produces a film that appears to be more or less uniform and continuous, increasing in thickness as the quantity of hydrogen sulphide is increased. The film is probably some form of lattice structure, the brown, peacock, and grey stains being the result of diffraction effects.

In the past, failure of benzoles to pass the copper-strip test was more frequently due to hydrogen sulphide than to elementary sulphur. The latter impurity is probably always co-existent with hydrogen sulphide, but corrosion inhibitors usually prevent its effect when hydrogen sulphide is removed. It has now become common practice to remove hydrogen sulphide from refined benzoles before storing.

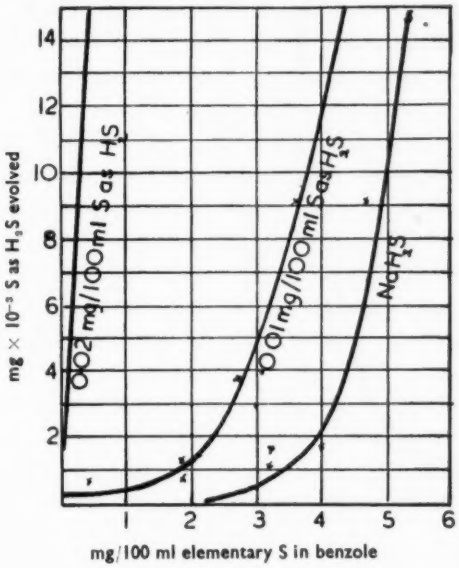

FIG. 2.

It was shown some time ago that when two benzoles, containing respectively hydrogen sulphide and elementary sulphur in amounts insufficient to produce corrosion, are mixed, a corrosive benzole may result. This phenomenon is of considerable importance, because a maker, finding his benzole satisfactory by the copper-strip test, may decide, quite reasonably, that further treatment for the removal of hydrogen sulphide is an unnecessary expense. When this benzole is blended with another benzole, however, corrosion may result. Also, even if hydrogen sulphide has been removed, the action of the widely spread bacterial organism known as *vibrio desulphuricans*, which reduces sulphates to hydrogen sulphide, may produce this substance from the water in the storage-tank bottom and thus contaminate the benzole.

This phenomenon of mutual activation of corrosion has now been investi-

gated quantitatively by the test described above, and the effect is well illustrated in Figs. 2 and 3. The limit of 2×10^{-3} mg of sulphur as hydrogen sulphide evolved from the treated copper strip, chosen as the boundary between pass and fail, corresponds for most benzoles with the production of a strip showing not more than a slight stain. It will be noticed that the presence of 0·01 mg per 100 ml of sulphur as hydrogen sulphide approximately halves the amount of elementary sulphur that can be tolerated without harm when no hydrogen sulphide is present. With neither benzole, however, does this quantity of hydrogen sulphide cause trouble when the elementary sulphur is absent.

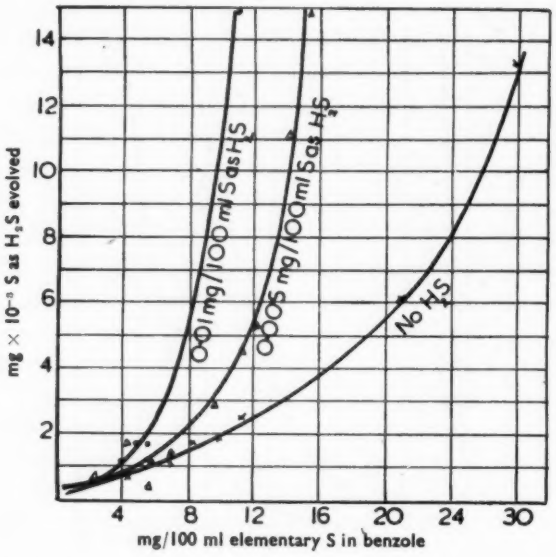

FIG. 3.

The mechanism of this mutual activation is not understood, but it is suggested that the uniform covering of sulphide produced by hydrogen sulphide provides nuclei on which the sulphide produced by elementary sulphur can grow.

(c) *The Effect of Corrosion Inhibitors.*

As already mentioned, certain naturally occurring impurities in refined benzoles and petrols act as corrosion inhibitors and may prevent the attack of copper by elementary sulphur. Thus there is no numerical relationship between the amount of corrosion and the amount of elementary sulphur present. A sample containing ten or more milligrams of elementary sulphur per hundred millilitres may produce no more corrosion than a sample containing less than one milligram per hundred millilitres. Even when corrosion has been initiated, the relationship between corrosion and

quantity is not linear (Figs. 2 and 3). The corrosion by hydrogen sulphide does not appear to be susceptible to the action of inhibitors to any great extent.

(i) *The Nature of Corrosion Inhibitors.* Although the action of corrosion inhibitors has long been known, information concerning their nature is scanty. Acids [10] and peroxides [11] have been demonstrated to have the effect, but other substances may also inhibit. Substances such as turpentine, amylene, and tetrahydronaphthaline, which readily form peroxides [12] and certain esters,[13] have been patented for use as corrosion inhibitors in benzole and petrols, although their use does not seem desirable from the point of view of gum stability. Samples of benzole that inhibit are usually those that have been highly refined with acid and contain only negligible quantities of unsaturated hydrocarbons, as shown by the slight colour produced when they are shaken with 95 per cent w/v acid in the acid-wash test.

It has been shown, both by fractional distillation and fractional crystallization, that many samples that exhibit inhibiting properties contain *cyclo*pentadiene or its dimer. When freshly prepared, or freshly distilled, these benzoles are not inhibiting, but the property develops on storage, as shown by the results in Table II, which are for copper-strip tests on elementary sulphur solutions in a sample of coke-oven motor benzole.

TABLE II.

The Effects of Ageing on the Production of Corrosion Inhibitors.

Days stored.	Wt of S added, mg/100 ml.	Appearance of Cu strip.	mg × 10^{-3} of S as H_2S evolved from strip.	Remarks.
None	0	Bright	<1·0	Sample as received
	10	Grey	— *	
	20	Black scale	—	
None	0	Bright	<1·0	Sample shaken with
	10	Grey with blue	—	Hg prior to adding
	20	Black	—	S
15	0	Bright	<1·0	Sample shaken with
	10	Bright	7·5	Hg prior to adding
	20	Black spots	—	S
22	0	Bright	<1·0	Sample shaken with
	10	Bright	4·5	Hg prior to adding
	20	Black spots	—	S

* Where no figures are given the amount of hydrogen sulphide was too high to measure by the test.

Neither *cyclo*pentadiene, di*cyclo*pentadiene, nor peroxides could be detected in any of the samples mentioned in Table II, nor could these substances be detected in fractions removed by fractional crystallization. When 2 litres of the material was fractionated through a column of 65 theoretical plates, however, the first fraction, distilling 43° to 70° C and representing 0·35 per cent w/w of the whole, was shown to contain about 0·05 per cent of *cyclo*pentadiene and the second fraction, distilling 70° to

75° C less than this quantity. It was confirmed that these fractions were causing the inhibition by adding them, after storage for four weeks, in a concentration of 10 per cent v/v to a sample of non-inhibiting pure benzole containing 10 mg per 100 ml of sulphur. It will be seen (Table III) that Fraction 1 prevents corrosion and Fraction 2 reduces it considerably.

TABLE III.

Sample.	Appearance of strip.	mg × 10^{-3} S as H_2S evolved from strip.
Benzole + 10 mg/100 ml S . . .	Black scale	Too great to measure
Benzole + 10% v/v Fraction 1 . .	Bright	<1·0
Benzole + 10% v/v Fraction 2 . .	Black at edges	Too great to measure

Neither Fraction 1 nor Fraction 2 gave a test for peroxides when tested with potassium iodide–starch reagent, even after storing for four weeks.

In order to give further confirmation of the effect of *cyclo*pentadiene and di*cyclo*pentadiene on copper corrosion, various amounts of the monomer, aged and fresh dimer, and dimer that had been treated with gaseous oxygen at 50° C for 3 hr, were added to solutions containing 10 mg per 100 ml of elementary sulphur in pure, non-inhibiting benzole. Fresh monomer or dimer showed some inhibiting properties when they were present in a concentration of 1 to 2 per cent v/v. The amount of di*cyclo*pentadiene required to inhibit the corrosion increased as the purity of the dimer was increased, thus suggesting that the active material was present as an impurity. Aged and oxidized dimer, however, showed strong inhibiting properties (Table IV).

TABLE IV.

Pure Benzole Containing 10 mg per 100 ml Elementary Sulphur.

Inhibitor.	Quantity, % v/v.	Appearance of strip.	mg × 10^{-3} as H_2S evolved from strip.
*Cyclo*pentadiene	1·0	Speckled black	Too great to measure
	0·1	Black scale	Too great to measure
	0·01	Black scale	Too great to measure
Di*cyclo*pentadiene (aged)	1·0	Bright	1·0
	0·6	Bright	4·0
	0·5	Bright	4·5
	0·2	Black spots	Too great to measure
	0·1	Speckled black	Too great to measure
	0·01	Black scale	Too great to measure
Fresh di*cyclo*pentadiene	2·0	Bright	0·0
	1·0	Black patches	Too great to measure
	0·7	Black patches	Too great to measure
	0·5	Black patches	Too great to measure
	0·2	Black scale	Too great to measure
Oxidized di*cyclo*pentadiene (contains peroxides)	1·0	Bright	2·0
	0·1	Bright	2·5
	0·04	Bright	7·0
	0·03	Slight grey patches	9·0
	0·02	Grey spots	Too great to measure
	0·01	Black patches	Too great to measure

Although peroxides could not be detected in the sample of stored motor benzole, the strong inhibiting action of oxidized di*cyclo*pentadiene, containing peroxides, indicates that these substances may be the active inhibitors. If this is so, however, very small quantities of the peroxides must be required to cause inhibition. This was further demonstrated by storing, in vented glass bottles, samples of a non-inhibiting benzole containing 10 mg per 100 ml of elementary sulphur and 0·5 per cent vol of *cyclo*pentadiene or di*cyclo*pentadiene. Further samples also contain 0·05 per cent cresol (Table V). All the solutions produced black strips when fresh, but eventually they became inhibiting. The cresol had the effect of arresting the formation of the corrosion inhibitor. Peroxides could only be detected in the *cyclo*pentadiene solution containing no cresol.

TABLE V.

Benzole Containing 10 mg per 100 ml Elementary Sulphur.

Days stored.	Addition.	Appearance of strip.	mg × 10^{-3} S as H_2S evolved from strip
None	0·5% v/v *cyclo*pentadiene	Black scale	Too great to measure
2		Black scale	Too great to measure
4		Black scale	Too great to measure
6		Brown	4·5
8		Slight brown	1·0
11		Bright	0·0
13		Bright	0·0
None	0·5% v/v *cyclo*pentadiene + 0·05% cresol	Black scale	Too great to measure
2		Black scale	Too great to measure
4		Black scale	Too great to measure
6		Black spots	Too great to measure
8		Slight brown	1·0
11		Slight brown	0·5
13		Slight brown	0·0
16		Slight brown	0·0
None	0·5% v/v di*cyclo*pentadiene	Black scale	Too great to measure
2		Black scale	Too great to measure
4		Black patches	Too great to measure
6		Peacock	5·0
8		Brown	2·5
11		Brown	0·5
13		Brown	0·5
16		Bright	0·0
None	0·5% v/v di*cyclo*pentadiene + 0·05% cresol	Black scale	Too great to measure
2		Black scale	Too great to measure
4		Slight peacock	16·0
6		Brown and blue	2·0
8		Brown	4·5
11		Brown and blue	4·0
13		Brown	2·0
16		Bright	0·0

Both fresh and oxidized di*cyclo*pentadiene also have a slight inhibiting effect towards solutions of hydrogen sulphide. Considerably more of the latter inhibitor was needed to prevent corrosion, which, in both experiments was only slight, due to the low concentrations of hydrogen sulphide used (Table VI).

TABLE VI.

The Effect of Corrosion Inhibitors on Corrosion by Hydrogen Sulphide.

A. Solution of pure benzole containing 0·04 mg S as H_2S per 100 ml.

Fresh di*cyclo*pentadiene, % v/v added.	Appearance of strip.	mg × 10^{-3} as H_2S evolved from strip.
0·9	Bright	0·0
0·8	Bright	0·0
0·7	Very slight brown	0·5
0·6	Slight brown	0·5
0·5	Brown	0·5
None	Peacock	9·0

B. Solution of pure benzole containing hydrogen sulphide.

mg/100 ml S as H_2S.	Appearance of strip.		mg × 10^{-3} S as H_2S evolved from strip.	
	No corrosion inhibitor.	+0·5% v/v oxidized di-*cyclo*pentadiene.	No corrosion inhibitor.	+0·5% v/v oxidized di-*cyclo*pentadiene.
0·002	Brown-blue	Bright	7·0	0·5
0·032	Blue	Brown	9·5	7·0
0·043	Grey-blue	Brown	10·5	6·0

That *cyclo*pentadiene or its dimer should exist in well-refined benzole fractions that have been subjected to treatment with concentrated acid during their manufacture, is somewhat surprising at first view. The benzene fraction, which is by far the greatest one from crude benzole, is almost free from unsaturated hydrocarbons. When pure benzoles are being made, therefore, it is only necessary to reduce, but not entirely remove, the unsaturated hydrocarbons in the small intermediate fractions not separated by the distillation, so that they do not contaminate the bulk of the benzene to an extent in excess of specification requirements. Usually the whole crude benzole is treated and the di*cyclo*pentadiene, which is less reactive than the monomer, may escape complete destruction. Any remaining may reappear, by depolymerization, in the benzene fraction.

(ii) *The Mechanism of Inhibition.* The mechanism of inhibition of the corrosion of copper by elementary sulphur is not understood. The effect, however, is not due to destruction of the elementary sulphur by the inhibitor. This was shown by treating a copper strip, first in a benzole that contained inhibitor but no sulphur, and afterwards in a solution of sulphur in a benzole that would corrode a fresh copper strip. The treated copper strip failed to corrode in the sulphur solution (Table VII).

A microscopic examination of the surface of strips treated in inhibiting benzoles in this way does not disclose any alteration to the surface.

Further confirmation that the inhibiting effect was not due in any way to the interaction of elementary sulphur and di*cyclo*pentadiene or its peroxide during storage was afforded by adding *cyclo*pentadiene to a non-inhibiting benzole and storing the mixture, elementary sulphur being added to portions

taken out during the course of the storage. At first no inhibition took place, but at the end of about 14 days, the addition of 10 mg of sulphur to the stored sample made little difference to a copper strip under the conditions of the test.

TABLE VII.

Pure Benzole Solution Containing 0·6 mg per 100 ml Elementary Sulphur.

mg × 10^{-3} S as H_2S evolved from copper strip.	
New, clean strip.	Strip previously treated for 2 hr in sulphur-free, inhibiting benzole.
12·0	<1·0

CONCLUSION.

The experiments described above are of theoretical rather than practical value, but they shed considerable light on the interpretation of the copper-strip test and on the precautions necessary, in storing fuels, to ensure that corrosiveness does not develop. An explanation is also afforded as to why a corrosive sample may show the reverse effect and become non-corrosive during storage.

ACKNOWLEDGMENT.

The authors desire to thank the Executive Committee of The National Benzole Association for permission to publish this work.

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ALKYLNAPHTHALENES. PART V. DETERMINATION IN TRINIDAD PETROLEUM.

By K. C. Bryant, G. T. Kennedy, and Miss E. M. Tanner.

Summary.

The use of specific dispersion measurements for the determination of naphthalene and its lower homologues in straight-run gas oil is described and its limitations are discussed.

The distribution of naphthalene and the methylnaphthalenes in a series of fractions from a vacuum distillation of a Trinidad gas oil, and the total amounts present in the crude oil have been determined by the ultra-violet spectroscopic method. The results are compared with those obtained by the specific-dispersion method and with those from earlier work on another gas oil.

Introduction.

The methods of determination of naphthalene and its homologues in petroleum fractions have been reviewed by Burdett and Gordon,[1] who developed a technique using polarographic reduction. To the use of specific dispersion, combined with an independent measurement of total aromatics, they advanced the following objections :—

(1) " . . . the presence of large amounts of olefins would introduce a serious error because of their co-extraction with aromatics."

(2) " A suitable base figure for the saturate portion of a sample could not be obtained without a time-consuming percolation over silica gel to remove the aromatics and olefins."

However, in the case of straight-run products, which are virtually free from olefins, the first objection does not apply, and since reference to the published data shows that the specific dispersion of the saturated portion can be predicted with fair accuracy, the second objection is hardly valid. Burdett and Gordon also considered the differences in ultra-violet absorption of naphthalene and the methylnaphthalenes inadequate for use in analysis. Nevertheless, a method based on these differences is well established.[2,3]

The accuracy obtained by the specific-dispersion method is not high, as will be seen from the graphs and results given below. It is shown that the main factors limiting the accuracy and applicability of the method are inherent uncertainties, independent of the accuracy of the experimental measurements. Within its limits, however, the method is useful in giving a semi-quantitative estimate of naphthalene derivatives, by a technique requiring only standard routine apparatus.

The Use of Specific Dispersion.

Specific dispersion, S, is defined by the equation

$$S = \frac{n_F - n_C}{d_4^{20}} \times 10^4$$

where n_F and n_C are the refractive indices of the material for the hydrogen F and C lines at the same temperature (20° C), and d_4^{20} has its usual significance.

It has been established experimentally [4] for some time that :—

(*a*) All saturated hydrocarbons, both paraffinic and naphthenic, mono- and poly-cyclic, have a practically constant specific dispersion of about 98, independent of their molecular weight (and hence of their boiling point).

(*b*) The specific dispersions of the mononuclear aromatics are considerably higher, and vary slightly with the length and number of the hydrocarbon side chains. The values lie in the range 150 to 170 for aromatics boiling between 200° and 250° C.

(*c*) Aromatic hydrocarbons with fused benzene rings have still higher specific dispersions.[5] For the homologues of naphthalene boiling about 220° to 280° C the values lie roughly between 250 and 270, varying with the length and number of side chains.

The considerable differences between the specific dispersions of saturated and aromatic hydrocarbons have been applied to the determination of the latter [4] in the boiling range below 200° C. However, the extension to the estimation of naphthalene derivatives in material boiling above 200° C has not been described, though the possibility has been recognized.[1]

It was shown by Grosse and Wackher [4] that the variation of specific dispersion with aromatic content by weight is very nearly linear. Hence, knowing the value of S for the sample, and for the aromatics present, or likely to be present, the weight percentage of aromatics in the sample can be found in the absence of naphthalenes or more condensed systems. Conversely, if the aromatic content is known from an independent determination (*e.g.*, by the aniline-point method) the average specific dispersion of the aromatics present can be found.

Furthermore, if the method is applied to a heavier fraction of known narrow boiling range, containing mononuclear aromatics and naphthalenes, the weight percentage of naphthalene compounds can be calculated, provided that the total aromatic content by weight, and the specific dispersions S_B and S_N of the benzene and naphthalene compounds respectively, are known.

The following equation can then be set up :—

$$100\,S_F = S_P P + S_B B + S_N N$$

where P, B, and N are the percentages by weight of saturated non-aromatics, mononuclear aromatics, and naphthalene derivatives respectively, and S_F is the specific dispersion of the fraction. S_P may be taken as 98·4, the total aromatic content $(B + N)$ is determined independently, and since $P + B + N = 100$

$$100S_F = 98{\cdot}4P + (100 - P - N)S_B + S_N N$$

and

$$N = [100(S_F - S_B) + \mathrm{P}(S_B - 98{\cdot}4)]/(S_N - S_B)$$

It follows that the accuracy of the figure obtained for the naphthalene

derivative N depends not only on the experimental accuracy, but also on the values selected for S_N and S_B.

If the data in the literature for the specific dispersion of mononuclear aromatic compounds [4, 5, 6] are plotted (after Grosse and Wackher) against boiling point, almost all the points lie within the area formed by the curves through the points for the mono-alkylbenzenes, at the bottom, and for the polymethyl-benzenes at the top.* Of compounds with approximately the same boiling point, those with the larger number of side chains lie near the polymethylbenzene curve. *Cyclo*alkylbenzenes and tetralin derivatives also lie in that area, the latter close to the polymethylbenzene curve.

Literature data [5, 6, 7, 8] indicate that a similar situation to that in the benzene series occurs with naphthalene derivatives.

A further complication is encountered with fractions boiling above 250° C in which diphenyls and diphenylalkanes may occur. The meagre literature data [6] indicate that diphenyls have specific dispersions similar to those of the monoalkylnaphthalenes, while those of the diphenylalkanes are nearer to those of the polymethylbenzenes. Results obtained in the boiling range above 250° C must therefore be interpreted with caution unless the presence of diphenyls and diphenylalkanes can be excluded.

Since sulphur compounds occur in gas oil, corrections dependent on their type and concentration should be applied. This latter information is seldom available, and as the sulphur content is generally low, neglect of this factor is not serious.

In view of the above limitations the method was applied only to fractions of narrow boiling range (2° to 4° C), where the naphthalene derivatives could be limited to naphthalene, methyl- and dimethyl-naphthalenes. For this purpose, the value taken for S_P was 98·4, and for S_N that of naphthalene (300), methylnaphthalene (294), or dimethylnaphthalene (280, with a small correction for possible ethylnaphthalenes), depending on the boiling point of the fraction.[6] The dispersion was calculated from measurements made on a Bellingham and Stanley Abbe refractometer, using white light, and densities were determined by the use of calibrated hydrometers. The use of a precision refractometer, such as a Pulfrich, would give more accurate values of dispersion without, however, necessarily yielding a more accurate final result (*vide supra*). The total aromatic content was taken as the mean of the values obtained from the aniline-point method (using the equation, percentage aromatic by volume $= 1{\cdot}29\Delta t$), and from the volume decrease on aromatic removal by acid washing (after conversion to a weight basis). From the plot of specific dispersion against boiling point for the mononuclear aromatics the highest and lowest values of S_B were read at the boiling point of the fraction, and the two extreme values for the percentage of naphthalene derivative, between which the true value should lie, were then calculated.

Ultra-violet Absorption.

The analyses for naphthalene, α- and β-methylnaphthalene were carried out by the method described elsewhere,[2, 3] using a Hilger E.498 medium quartz spectrograph and a Spekker spectrophotometer.

* The authors wish to acknowledge that this was first pointed out to them by Dr A. Newton.

In comparing the several methods [1] it should be noted that only the spectroscopic method gives the relative proportions of α- and β-methylnaphthalenes, and that while the accuracy of the specific-dispersion method falls off sharply as the concentration of naphthalene derivative diminishes, that of the spectroscopic method is almost independent of the naphthalene concentration.

The ultra-violet spectra of the dimethylnaphthalenes [9] and the ethylnaphthalenes have been determined, but the similarity of the spectra precludes any quantitative analysis of mixtures without further information as to the isomers present. However, the presence of 2 : 6-dimethylnaphthalene in gas-oil fractions was shown by its spectrum, and confirmed by its isolation from a picric-acid extract.

Results.

These methods have been applied to the fractions obtained by the vacuum distillation of a Trinidad high-octane gas oil.* 75 gal were charged to a

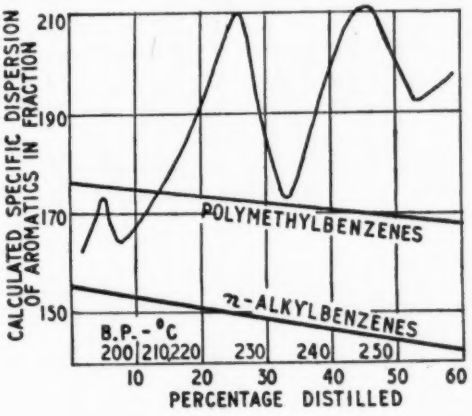

Fig. 1.

pilot-plant fractionation unit with a column containing 10 ft of 6-in-diameter Stedman packing.[10] The distillation was carried out at a pressure of 50 mm Hg until 55 per cent of the charge had been taken overhead, when the pressure was lowered to 30 mm to keep the reboiler temperature below 300° C and thus avoid cracking. A reflux ratio of approximately 30 : 1 was maintained throughout, and distillate fractions each of volume about 0·5 per cent of the charge were collected. Their boiling points were determined on a laboratory Cottrell apparatus.

The total percentage of aromatics by weight and the specific dispersion of each fraction were then determined, from which the average specific

* The terms "high octane" and "low octane" are used to characterize certain blended Trinidad crudes by reference to engine performance of the gasoline fraction from them.

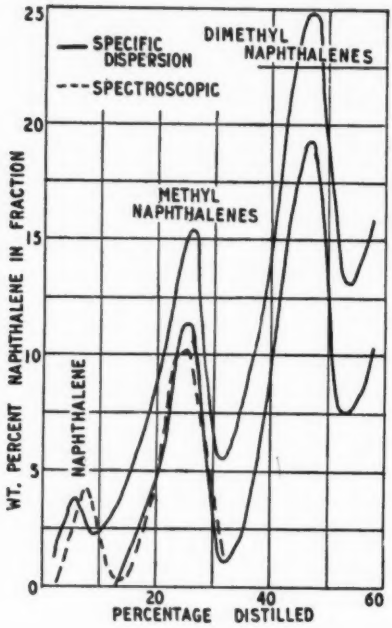
SPECIFIC DISPERSION
SPECTROSCOPIC
DIMETHYL NAPHTHALENES
METHYL NAPHTHALENES
NAPHTHALENE
WT. PERCENT NAPHTHALENE IN FRACTION
PERCENTAGE DISTILLED
0
5
10
15
20
25
20
40
60

FIG. 2.

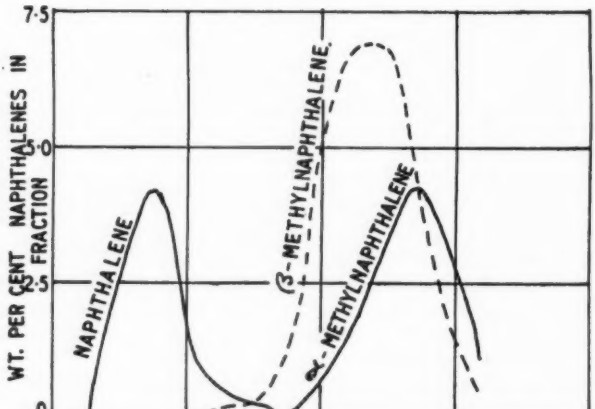
NAPHTHALENE
β-METHYLNAPHTHALENE
α-METHYLNAPHTHALENE
WT. PER CENT NAPHTHALENES IN FRACTION
PERCENTAGE DISTILLED
0
2·5
5·0
7·5
10
20
30
40

FIG. 3.

dispersion of the aromatics in each fraction was calculated. These results are shown in Fig. 1. The straight lines show the values assumed for the monoalkyl- and polymethyl-benzenes. Using the values read from these lines, the extreme percentages of naphthalene derivatives were calculated as detailed above and the mean value taken. In Fig. 2 these values are compared with those determined spectroscopically for naphthalene and the methylnaphthalenes. In Fig. 3 the distribution of naphthalene and the methylnaphthalenes in the high-octane gas oil is shown.

The percentages of naphthalene, methyl- and dimethyl-naphthalenes in high-octane gas oil and crude oil are shown in Table I. These values are

TABLE I.

	Wt % in gas oil.		
	High octane.		Low octane.
	Specific dispersion.	Spectroscopic.	Spectroscopic.
Naphthalene	0·1 ± 0·1	0·23 ± 0·01	0·12 ± 0·01
α-Methylnaphthalene	1·41 ± 0·5	0·31 ± 0·02	0·42 ± 0·02
β- ,, ,,		0·64 ± 0·03	0·76 ± 0·03
Dimethylnaphthalenes	2·93 ± 0·6		

	Wt % in crude oil.	
	High octane.	
	Specific dispersion.	Spectroscopic.
Naphthalene	0·02 ± 0·02	0·046 ± 0·002
α-Methylnaphthalene	0·28 ± 0·1	0·062 ± 0·003
β- ,, ,,		0·128 ± 0·006
Dimethylnaphthalenes	0·59 ± 0·1	

compared with those previously obtained by the spectroscopic method on low-octane gas-oil fractions. It will be observed that they are of the same order of magnitude as those found in an American crude oil.[11] In particular, the predominance of β-methylnaphthalene may be noted.

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